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Dynamics of CO chemisorption on a metal cluster

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The understanding of the dynamics of collisions between molecules and small metal clusters is an important component of a general understanding of practical heterogeneous catalytic processes. We report here quasiclassical trajectory studies of CO colliding with a five-atom metal cluster, with our primary focus being on the modeling of collisions with a copper cluster. Since the forces in these systems are still largely unknown, we have considered a number of simple potential-energy parametrizations so as to determine the range of behavior which might be expected. In general, CO is found to add readily to the metal cluster, forming a complex which is stable on the time scale of the trajectories. The effects of variations in the cluster geometry and extensions to systems having higher molecule-cluster binding energies are also considered here, as is the question of whether or not there is a significant distortion of the metal cluster geometry upon addition of CO. This last topic is conveniently approached via a combination of trajectory and Monte Carlo simulated annealing techniques.

I. INTRODUCTION

Most of the detailed fluid-surface dynamics studies reported to date have involved the use of either single-crystal surfaces or polycrystalline surfaces which locally behave as if they are single crystals. By examining surfaces such as these, workers have clarified numerous facets of surface reactivity, the extensive investigations focusing on the mechanism of the hydrogenation of hydrocarbons¹ being just one example of the sort of work which has received a great deal of attention. From a practical standpoint, though, one must recognize that actual industrial catalytic processes do not make use of single-crystal surfaces, and in fact one commonly finds that practical catalysts consist of very small metal or metal oxide particles supported on an unreactive substrate, often alumina or silica.² The great advantage of this arrangement is that the active catalytic species is highly dispersed, i.e., the active atoms are located primarily at surface rather than catalytically inaccessible bulk sites.³ High dispersion obviously is of particular importance when precious metal catalysts are involved and the cost of the material clearly is an important consideration. (Large-scale industrial processes do not represent the only applications of these catalysts either. For example, it is known that in the conventional photographic process the latent image consists of small clusters of silver atoms which, during development, catalyze the reduction of the supporting silver halide microcrystals.⁴) The smallest of these particles ($< 15 \text{ \AA}$) also may behave quite differently than do either isolated metal atoms or larger crystallites (and certainly differently than do bulk metals). It has been proposed that very highly dispersed particles may even exhibit a combination of the best properties of conventional heterogeneous and homogeneous catalysts, that is, both high activity *and* high selectivity.² The preparation of these catalytic particles by the stripping of ligands from organometallic cluster compounds which do not contain halogens may also provide a strategy for skirting the problems of poisoning and accelerated aggregation which

can accompany the presence of halides. Furthermore, the fact that in the majority of metal clusters the metal atoms are already in a zero-valent state has been cited as a reason for hoping that such catalysts might be activated under relatively mild reaction conditions, since the usual preparative step consisting of a high-temperature hydrogen reduction of the metal atoms would be unnecessary. Thus, it ultimately may prove far more fruitful to focus one's attention on catalytic surfaces which are composed of microcrystals or metal (metal oxide) clusters rather than those made up of atomic planes. (But in doing so, one should not ignore the relationship between dynamics and reactivity at cluster surfaces and the corresponding processes at single-crystal surfaces inasmuch as it is for these latter systems that we already have a limited insight into some of the mechanistic details.)

The potential advances in the understanding of heterogeneous catalysis to be gained from the study of the structure, dynamics, and reactivity of small metal clusters by no means have gone unrecognized. Perhaps the greatest stimulus to the field overall was provided by Muetterties and co-workers,⁵ who developed and defined the limits of the analogy between the structure and bonding properties of chemisorbed species and those same properties observed in solution-phase organometallic cluster compounds. (A highly recommended introduction to the extensive body of work motivated by the exploitation of this analogy is the recent text by Albert and Yates.⁶) Also instrumental in spurring interest in the study of cluster systems, though, has been the refinement of experimental techniques for the production of size-selected bare-metal clusters (both neutrals and ions) in expansion beams and for the reaction of these clusters with molecules under controlled conditions.^{7,8} These techniques, as well as complementary methods such as low-temperature matrix stabilization⁹ and vacuum deposition¹⁰ and also various spectroscopic and scattering probes [e.g., extended x-ray absorption fine structure^{11,12} (EXAFS) and electron diffraction¹³], are now yielding a wealth of information, especially with respect to what Boudart *et al.*¹⁴ has termed the "structure-sensitive" (particle-size dependent) aspects

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of metal catalysis. To give just one striking example, we note the work of Riley and co-workers,¹⁵ as well as that of others,^{16,17} which has shown there to be a variation by 4 orders of magnitude in the rates of the reaction of H_2 and D_2 with Fe_x ($x = 6-68$).

Coincidentally with the burgeoning of experimental interest in these systems, a number of theory groups have turned their attention to the characterization of small clusters.¹⁸ Initially, the work primarily was pursued with the goal of modeling adsorption on single-crystal surfaces,¹⁹ but it is now fairly clear that, despite the hopes engendered by early results of semiempirical theories,²⁰ often even the inclusion of tens of metal atoms is insufficient for the reproduction of bulk metal properties.²¹ But the structures and binding energies of clusters themselves also have attracted a great deal of interest, in part due to the fact that performing *ab initio* self-consistent-field (SCF) calculations on even relatively small metal aggregates (especially, those involving transition metals) requires one to work at the practical limits of modern computational techniques. Due to the difficulties in describing the chemistry of transition-metal clusters via such methods, several workers have concentrated instead on somewhat simpler systems such as Be_x ,²² Al_x ,^{23,24} and Li_x and other alkali-metal clusters,²⁵ in which the bonding involves primarily *s* and *p* orbitals. Several potential-energy parametrizations also have appeared. For predicting equilibrium cluster geometries, a relatively simple potential function comprising sums of two-body Lennard-Jones terms and three-body Axilrod-Teller functions²⁶⁻²⁹ has proved to date to be the most successful.

Very little information is available, however, concerning the detailed dynamics of atom-metal cluster (or molecule-metal cluster) reactions. Most of the published dynamical studies have dealt instead with the kinetics of nonmetal cluster formation or dissociation,^{30,31} the goal in these investigations being the understanding of mechanisms of atmospheric nucleation,^{32,33} or aerosol formation and dissipation.³³ In a few cases we do have some inkling of the chemisorption processes occurring at cluster surfaces based on the identity of the adsorbate. Just such a case is the chemisorption of ethylene on supported Pt, Rh, Pd, and Ru particles, which has been investigated by Beebe and Yates³⁴ using transmission infrared spectroscopy. They were able to identify ethylidyne as being the ultimate absorbed species on all of these particles. (In addition, they observed a breakdown of the ordinary surface-dipole selection rule,^{35,36} which normally limits one's ability to observe vibrational modes that involve a change in the dipole moment parallel to a polarizable surface plane, in accordance with the predictions of Greenler and co-workers³⁶ for very small clusters. Thus, the spectroscopy of cluster-bound species may be more revealing with regard to the details of molecule-surface bonding than are the analogous measurements made on species bound to crystal surfaces.) Jarrold and Bower³⁷ also have observed the reaction of ethylene, this time with Al_x ($x = 24-26$) clusters by means of a low-energy ion-beam method, and have reported the existence of three distinct bound hydrocarbon species, only one of which involves the loss of a hydrogen atom. But in neither of these examples

does one find much insight into the detailed energetics that actually leads to the formation of specific products.

Nearly nothing is known about how energy transfer and disposition affect the probability of adsorption in these atom-metal cluster or molecule-metal cluster systems, or, more generally, about the relationship between the topology of the potential-energy hypersurface and reactivity. Even the answer to the question of whether electronic or geometric effects are more important in determining variations in reactivity with cluster size, while actively pursued,^{15 38-40} is as yet uncertain. The present work represents an initial attempt to address some of these questions via a characterization of the dynamics in particularly simple molecule-metal cluster systems, focusing principally on $CO-Cu_x$. We believe that systems such as these are best approached via classical (or quasiclassical) techniques. They are sufficiently large that one at present cannot hope to describe them adequately through quantum-mechanical scattering theory (unless the scope of the work is severely restricted to dimers or, perhaps, trimers, the number of energetically accessible product channels can be too large to manage), and yet they do not exhibit the long-range periodicity (as do single-crystal surfaces) which can dramatically simplify the analysis.

Of all the metal cluster species investigated, surely Cu_x clusters are among the most popular for study.⁴¹ The early interest in polynuclear (primarily diatomic) copper species derived in part from the relative ease with which they could be prepared by vaporization in a furnace and then studied spectroscopically. Improvements in technology introduced by Smalley and co-workers⁸ for the controlled production of small, cold clusters (involving a high-power laser vaporization within a supersonic nozzle) and the widespread use of modern laser-based detection techniques have led to the present relatively good models of the physical structure of the smallest clusters as well as some understanding of their electronic structures.⁴¹ Certain properties of the larger copper clusters also have been reported using a variety of experimental methods. Relevant to the present inquiry are ESR studies of the species Cu_5 , which have suggested a distorted trigonal-bipyramidal structure for the cluster,⁴² while EXAFS investigations of several small copper clusters¹² have revealed a contraction of the interatomic distances as compared with the values for bulk copper. (While this last result is consistent with the findings in a variety of other metal clusters, it disagrees with an earlier analysis of electron diffraction results which indicated no such contraction.⁴³) Measurements also have been reported of cluster ionization thresholds⁴⁴ and electron affinities⁴⁵ for a very wide range of cluster sizes. Particularly noteworthy is the observation that for the small clusters, those containing an even number of atoms have a higher ionization threshold than the adjacent odd clusters, while the opposite trend, which persists to larger clusters, is seen for the electron affinities (i.e., they are in general lower for the even clusters). In both cases, however, the bulk copper values are not realized even for clusters containing as many as 25 atoms.

An experimental study of the $CO-Cu_x$ system has been reported by Cox *et al.*⁴⁶ as part of an extensive survey of CO chemisorption on metal clusters. They determined relative

chemisorption probabilities for Cu_x ($x = 1-14$) clusters, but due to the fact that their experiment did not show a peak corresponding to $\text{Cu}_x(\text{CO})_y$ in the mass spectrometer but only a decrease in the bare-cluster signal, they were unable to ascertain how many molecules attached to the clusters. Notable is their observation that two clusters, Cu_7 and Cu_{13} , exhibit reactivities that are only about one-half of those reported for clusters containing one fewer or one more copper atom. Otherwise, no dramatic size-selective reactivity was observed.

We have chosen here to examine in detail the reaction between CO and a Cu_5 cluster. In a sense the use of a five-atom cluster in this initial investigation represents a compromise. Cu_5 is sufficiently small that fairly unambiguous structural information is available, and yet is large enough that it apparently displays a reactivity with CO which is typical of the larger (Cu_6 – Cu_{13}) clusters. In addition Bagus, Nelin, and Bauschlicher⁴⁷ have reported calculations of the binding energy and geometry of a CO– Cu_5 cluster. The cluster geometry assumed in their calculations was chosen so as to mimic CO binding to the (100) face of a copper single crystal, and thus does not represent the equilibrium gas-phase cluster geometry. But even so, the calculations provide us with a benchmark in our modeling of the forces in this system.

II. CALCULATIONS

A. Potential-energy function

The expression which we have used for the potential energy of CO interacting with a copper cluster is a slight modification of a simple functional form suggested by Baetzold.⁴⁸ In this model the carbon–copper interactions (as well as the CO diatomic potential) are described by Morse potentials, while the oxygen–copper interactions are given by repulsive exponential Born–Mayer potentials. This choice of potential function successfully reproduces the observed bonding geometry of CO on a solid surface, namely that the molecule is bound perpendicularly to the surface with the oxygen atom directed away from the surface.⁶

Specifically,

$$V = V_{\text{CO}} + \sum_{i=1}^5 (V_{\text{CCu}_i} + V_{\text{OCu}_i}),$$

where

$$\begin{aligned} V_{\text{CO}} &= D_{\text{CO}} (e^{-2\beta_{\text{CO}}(r_{\text{CO}} - r_{\text{CO}}^0)} - 2e^{-\beta_{\text{CO}}(r_{\text{CO}} - r_{\text{CO}}^0)}), \\ V_{\text{CCu}_i} &= D_{\text{CCu}_i} (e^{-2\beta_{\text{CCu}_i}(r_{\text{CCu}_i} - r_{\text{CCu}_i}^0)} - 2e^{-\beta_{\text{CCu}_i}(r_{\text{CCu}_i} - r_{\text{CCu}_i}^0)}), \end{aligned} \quad (2.1)$$

and

$$V_{\text{OCu}_i} = V_{\text{OCu}} e^{-\alpha_{\text{OCu}}(r_{\text{OCu}_i} - r_{\text{OCu}}^0)}. \quad (2.2)$$

(The variables here have their usual meanings.) While the Morse parameters for CO are quite well known, the values of the potential parameters appropriate to the pairwise additive C–Cu and O–Cu interactions are highly uncertain. We have determined several sets of parameters by fitting the net CO-cluster binding energy and geometry to the complete active space SCF (CASSCF) results reported by Bagus, Nelin, and Bauschlicher⁴⁷ for CO bound to a Cu_5 cluster in the shape of

a square pyramid, with the carbon atom being bound directly to the apex copper atom such that the resulting structure is of C_{4v} symmetry. (See Fig. 1. The Cu–Cu distances are taken to be those observed for bulk copper and the C–O distance was fixed at its gas-phase value. Although Bagus, Nelin, and Bauschlicher also varied the C–O distance, their optimized value is very close to the experimental gas-phase bond length.) Since Eqs. (2.1) and (2.2) contain far more parameters than one is able to determine uniquely by fitting only to the overall CO-cluster bond energy and bond distance, there is an infinite number of parameter sets which might be proposed. Somewhat arbitrarily we have adopted the general values for the β and α parameters recommended by Baetzold⁴⁸ simply in order to reduce the number of free parameters, leaving thus only the overall scaling factors (D_{CCu} and V_{OCu}) and the r^0 values. The first three sets of these fitted parameters are given in Table I, all corresponding to different two-body interactions. In order to clarify the practical differences between these parameter sets, the terms $\sum_{i=1}^5 V_{\text{CCu}_i}$ and $\sum_{i=1}^5 V_{\text{OCu}_i}$, as well as the sum of these terms have been plotted vs the CO-cluster bond distance and are shown in Fig. 2. (Again, recall that we are dealing here with the constrained C_{4v} model cluster.) All three parameter sets reproduce reasonably well the 0.67 eV binding energy and 1.95 Å bond length predicted by Bagus, Nelin, and Bauschlicher,⁴⁷ the maximum deviations from the CASSCF results being 0.02 eV and 0.04 Å. In sets 1 and 2 the values of r_{CCu}^0 and r_{OCu}^0 are taken to have a single value, while in set 3 the r_{OCu}^0 is taken to be smaller than r_{CCu}^0 , and thus the net potential is more strongly dominated by the C–Cu Morse potential terms. Sets 1 and 2 differ chiefly in the strengths of the two-body interactions.

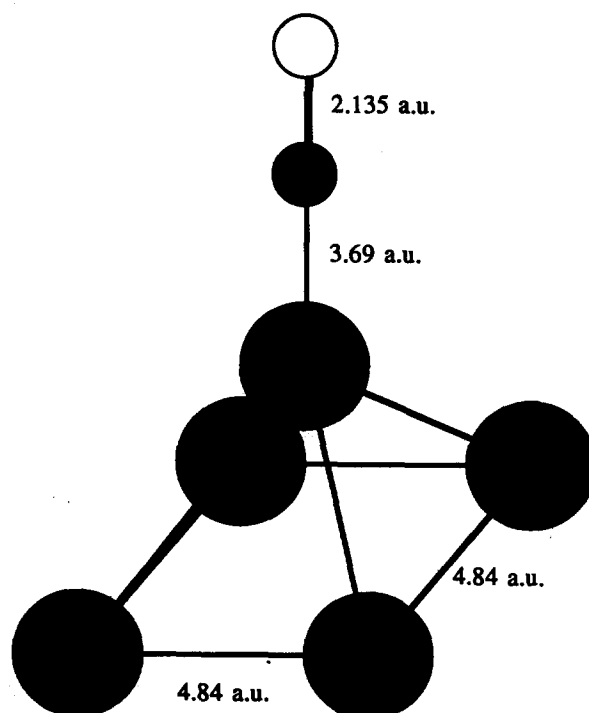


FIG. 1. C_{4v} cluster geometry used in the potential-energy parametrization. The gray circles represent copper atoms, the black one a carbon atom, and the unshaded one an oxygen atom.

TABLE I. Potential-energy parameters.

Parameter	Set				
	1	2	3	4	5
D_{CO} (eV)	11.108	(These values are held constant in all of the potential parametrizations.)			
β_{CO} (\AA^{-1})	2.311				
r_{CO} (\AA)	1.128				
ϵ (eV)	2.01				
r_0 (\AA)	2.22				
α_{OCu} (\AA^{-1})	2.7				
β_{CCu} (\AA^{-1})	1.8				
D_{CCu} (eV)	2.602	1.35	0.675	1.35	2.602
V_{OCu} (eV)	100.0	27.0	7.00	7.00	7.00
r_{CCu} (\AA)	1.25	1.60	1.90	1.90	1.90
r_{OCu} (\AA)	1.25	1.60	1.50	1.50	1.50

The potential-energy description of the system is completed by a specification of the Cu-Cu interactions. Here we have chosen to adopt a model function consisting of two- and three-body terms that has been used previously in several studies of equilibrium metal cluster geometries.²⁶⁻²⁹ Explicitly, we write the total cluster potential for N particles as

$$V_C = \sum_{i < j} U_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k),$$

where the two-body terms are taken to be standard Lennard-Jones 6-12 potentials,

$$U_2(\mathbf{r}_i, \mathbf{r}_j) = \epsilon [(r_0/r_{ij})^{12} - 2(r_0/r_{ij})^6],$$

and the three-body terms are taken to be Axilrod-Teller functions,

$$U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = Z \frac{1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k}{(r_{ij} r_{ik} r_{jk})^3}, \quad (2.3)$$

which describe interactions between three particles arranged in a triangle with sides of length r_{ij} , r_{ik} , r_{jk} and angles of magnitude θ_i , θ_j , θ_k . The role which three-body interactions play in the determination of cluster structure is easily investigated within this model through an adjustment of the scaling parameter Z . It actually is more convenient to recast Eq. (2.3) in a form which yields a dimensionless scaling parameter Z^* , defined by $Z^* = Z/\epsilon r_0^3$, so that now

$$U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = Z^* \epsilon r_0^3 \frac{1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k}{(r_{ij} r_{ik} r_{kl})^3}.$$

When $Z^* = 0$, the potential V_C , consisting then only of the pairwise-additive Lennard-Jones potentials, always leads to a close-packed cluster geometry. Halicioglu and White²⁸ have shown however, that nonzero values of Z^* can lead to a variety of equilibrium cluster geometries. For a five-atom cluster such as the one in which we are interested, the close-packed trigonal bipyramid (D_{3h}) is the lowest-energy structure whenever $Z^* < 0.45$, but when $0.45 < Z^* < 0.70$ the lowest-energy structure is a two-dimensional trapezoid (C_{2v}), when $0.70 < Z^* < 0.85$ the lowest-energy structure is a planar pentagon (D_{5h}), and when $Z^* > 0.85$ the lowest energy structure is linear ($D_{\infty h}$). The experimental evidence strongly suggests that the bipyramid structure is found for Cu_5 ,⁴² so Z^* should be taken to have a value less than

(roughly) 0.45. Calculations will be reported here using two different values of Z^* , 0.3 and 0.4, both of which might be appropriate for copper clusters. (A Z^* value of 0.3 has been used previously in studies of the structures of gold microclusters.²⁷) However, in an effort to make the present work somewhat more general in scope than just the dynamics of CO-Cu_5 , we also will report results from calculations which make use of a Z^* value of 0.5, the value which appears to yield accurate structural information for small aluminum clusters.^{26,29}

B. Trajectories

The procedure for generating thermal reactive cross sections (in the present case cross sections for the chemisorption of CO) from the results of quasiclassical trajectories is well documented,⁴⁹ and so we shall not reproduce it in detail here. Monte Carlo averaging over initial internal states of CO was carried out by means of the prescription of Porter, Raff, and Miller,⁵⁰ while the averaging over impact param-

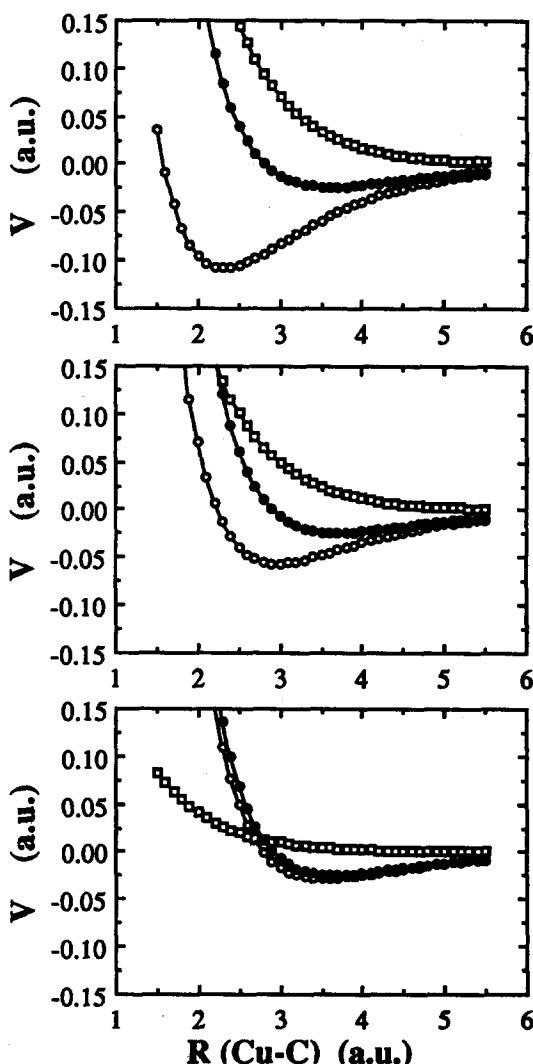


FIG. 2. Potential curves for CO-Cu_5 (C_{4v} geometry). The open circles are the sum of the C-Cu interactions, the open squares are the sum of the O-Cu interactions, and the solid circles are the sum of these two contributions. The top panel represents parameter set 1, the middle panel set 2, and the bottom panel set 3.

eters was implemented by means of a random selection of quantum numbers for the initial orbital angular momentum. (Maximum values of the impact parameter were selected on the basis of a separate nonstatistical calculation. The b_{\max} values determined in this way fell in the range 8–10 Å.) All calculations reported here correspond to an equilibrium system temperature of 400 K, which is the temperature that Cox *et al.*⁴⁶ believe appropriately characterizes their experiments.

The manner in which one selects initial conditions for the copper clusters themselves is problematical. One might proceed by performing a normal-mode analysis on a cluster and then assigning it an initial internal energy in the way one would for any large molecule.⁵¹ However, there is a growing body of evidence suggesting that cluster structures may be fluxional,⁵² and thus the determination of the normal modes in such a system may be ill defined. We consequently have chosen a purely classical approach to the problem of setting the initial conditions. First, we construct a thermally biased Monte Carlo random walk⁵³ of the isolated cluster at the given temperature, thereby generating a set of initial configuration snapshots. (The procedure here is nearly identical with the one we have used previously in determining initial conditions for a solid surface.⁵⁴) Starting from one of these initial sets of atomic positions and randomly selected initial momenta, we then calculate a short (0.1 ps) trajectory which produces an equilibration of the cluster. At the end of this short trajectory, any overall translation and rotation of the cluster is removed and the cluster center of mass is restored to the origin of our coordinate system.

The result of the above procedure is that the cluster atoms' positions and momenta are now appropriately initialized and so the CO collision trajectory can begin. Throughout these calculations (a single exception to this procedure is noted in Sec. IV) an integration step size of 4.0×10^{-4} ps was used with an Adams–Moulton fifth-order predictor, sixth-order corrector algorithm (started via a fourth-order Runge–Kutta–Gill algorithm), this step size yielding energy conservation to better than four decimal places over a 10 ps trajectory. A trajectory was terminated whenever either the separation between the CO and Cu₅ centers of mass exceeded some critical value (taken to be equal to b_{\max}) or the 10 ps time limit was reached. If, however, a trajectory displayed a CO–Cu₅ separation which was large, although less than the critical value, when the time limit was reached, that trajectory was integrated separately to a time limit of 20 ps to see if it was in fact chemisorbing or not. Analysis of the final state of the collision products was then carried out using standard methods.⁴⁹ The most important quantity obtained was the reactive cross section, which is given by the simple expression

$$\sigma_r = \pi b_{\max}^2 \left(\frac{N_r}{N} \right),$$

where b_{\max} is the maximum value of the impact parameter, N_r is the number of trajectories yielding bound CO–Cu₅, and N is the total number of trajectories, and the corresponding error in the cross section, which may be estimated using the formula

$$\Delta\sigma_r = \pi b_{\max}^2 \left(\frac{N_r}{N} \right) \left(\frac{N - N_r}{N_r N} \right)^{1/2} = \sigma_r \left(\frac{N - N_r}{N_r N} \right)^{1/2}.$$

It should be noted that the cross sections reported in the present work actually ought to be viewed as upper bounds to the true values in that we have not included in the calculations any correction factor which would account for the dissociation of a metastable CO–Cu₅ cluster on a time scale which is too short to be observed in the existing experiments but too long to be accessed via trajectories. From the results of those trajectories not leading to reaction, one may also compute scattering angle distributions, final CO internal state quantum numbers (although the separation of rotational and vibrational energy is, in general, ill defined, the quantum numbers may be defined uniquely as the nearest-integer values formed by inverting the angular momentum as a function of J_r in the case of rotation, and by solving the Wentzel–Kramers–Brillouin (WKB) phase integral in the case of vibration), final relative translational energy distributions, and copper cluster translational and (approximate) rotational energy distributions. From the reactive trajectories, one can calculate final CO–Cu₅ energy distributions and, if one assumes that the CO bond is dynamically isolated from the remainder of the cluster (it will, in general, be much higher in frequency than the other vibrational modes), then an approximate vibrational quantum number for the C–O stretching mode, again via the solution of a WKB phase integral. All results are reported on the basis of 500 trajectories per set of potential parameters.

C. Equilibrium geometries

While the work of Halicioglu and White²⁸ and others^{26,27,29} has illuminated the relationship between cluster potential parameters and cluster geometries, no studies have been made of the effect which a chemisorbed species has on the structure of the metal cluster. There are several different approaches which one might take in the determination of equilibrium cluster structures, but perhaps the simplest is the simulated annealing method proposed by Kirkpatrick, Gelatt, and Vecchi.⁵⁵ In this method one performs a Monte Carlo random walk with Metropolis sampling⁵³ starting at a (relatively) high temperature and periodically reducing the temperature which characterizes the walk until a suitably low temperature is reached. Essentially, one is just stepping down the system temperature in a fashion which allows for reequilibration at each intermediate temperature. Starting temperatures in our calculations were customarily in the range 1000–3000 K, with the final temperature in all cases being 1 K. (To confirm that the calculation has indeed reached a global minimum in the potential energy, we repeated the process with different initial temperatures and different numbers of equilibration steps per temperature. It is not inconceivable that a single random walk calculation can converge to a local rather than global energy minimum given a particular set of initial conditions.)

Although much insight can be gained from an examination of plots of cluster atom positions before and after the collision with CO, the assessment of the degree of deformation of the cluster as a result of chemisorption really requires

TABLE II. Reactive cross sections.

Parameter set	Z^*	σ_r (\AA^2)
1	0.400	124 ± 5
2	0.400	134 ± 4
3	0.400	167 ± 5
2 ("cold cluster")	0.400	136 ± 4
2	0.300	139 ± 6
2	0.500	148 ± 6
3	0.500	185 ± 6
4	0.400	191 ± 6
5(a)	0.400	198 ± 7
5(b)	0.400	156 ± 7

some quantitative measure of that deformation. A convenient measure is afforded by the cluster compactness parameter devised by Halicioglu and Pamuk²⁹ and defined via the expression

$$\gamma = N^{-1} \sum_i \sum_{j>i}^N (r_{ij}/r_0)^2, \quad (2.4)$$

where N is the number of cluster atoms ($N = 5$ in the present work), r_{ij} is the distance between metal atoms i and j , and r_0 is the two-body potential equilibrium bond distance. This expression actually differs slightly from the one suggested by Halicioglu and Pamuk in that theirs contains the cluster nearest-neighbor distance d_{nn} rather than r_0 . Either choice would be adequate here, but we find the one which involves r_0 to be particularly easy to employ. Even though the individual γ values calculated from a batch of trajectories exhibit a significant amount of scatter, average γ 's computed by averaging over the results of 50 trajectories appear to yield reliable estimates of the degree of cluster geometry change.

III. CO-Cu₅

In Table II we give the calculated cross sections for the chemisorption of CO on Cu₅ obtained using a number of different potential-energy descriptions. Let us first concentrate on the results obtained for parameter sets 1, 2, and 3 with $Z^* = 0.4$ (i.e., the first entries in the table). While the change in the cross section obtained going from set 1 to set 2 represents only an 8% increase, the change found in going from set 2 to set 3 is roughly 25%. Recall that sets 1 and 2 are very similar in that the ultimate binding potential is a tradeoff between the attractive C-Cu interactions and the repulsive O-Cu interactions (see Fig. 1). On the other hand, in set 3 the C-Cu₅ potential is the dominant contribution to the overall potential-energy surface. We therefore conclude that it is the relative diminution of the repulsive O-Cu contributions to the potential that is primarily responsible for the larger cross section calculated when using the third set of potential parameters.

The dynamical distinctions between sets 1 and 2 and set 3 also appear in a correlation of reactivity with impact parameter. One can see in the results displayed in Fig. 3 that far fewer of the small impact parameter collisions are nonreactive in the case of set 3 than for the other two parameter sets. This observation actually is quite consistent with the analy-

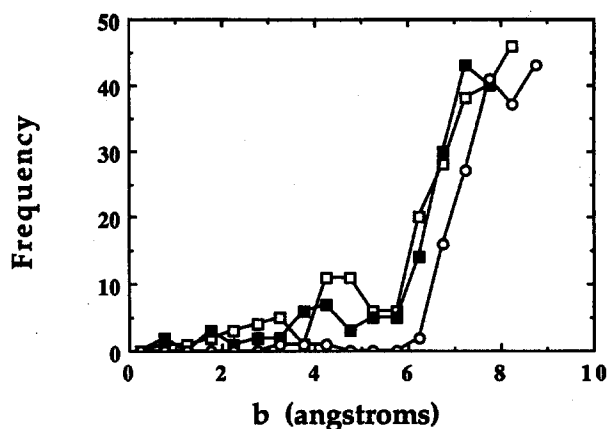


FIG. 3. Distribution of impact parameters for nonreactive collisions obtained using parameter set 1 (the open squares), set 2 (the solid squares), and set 3 (the open circles).

sis suggested above. A reduction in the contribution to the CO-cluster interaction from the repulsive forces between O and the Cu atoms makes it less likely that the CO molecule will collide with the cluster oxygen end first and be reflected from the cluster on a time scale which is sufficiently short that the CO cannot rotate into a position so as to yield a net attractive interaction. With fewer short-range repulsive O-cluster collisions, one also anticipates finding fewer nonreactive collisions leading to scattering through large angles. This result indeed may be seen in the scattering angle data displayed in Fig. 4. Another consequence of a reduced O-Cu repulsion is the lessening of the torque on the CO as the molecule approaches the cluster, such that nonreactive collisions should be less likely to involve a change in the CO rotational number. This result is in fact seen in our calculations. While for sets 1 and 2 we find that 35% and 41%, respectively, of the nonreactive trajectories are characterized by $\Delta J \neq 0$, only 9% of those obtained using set 3 show a change in J . Other properties, however, which depend only on the net CO-cluster interaction, show no obvious differ-

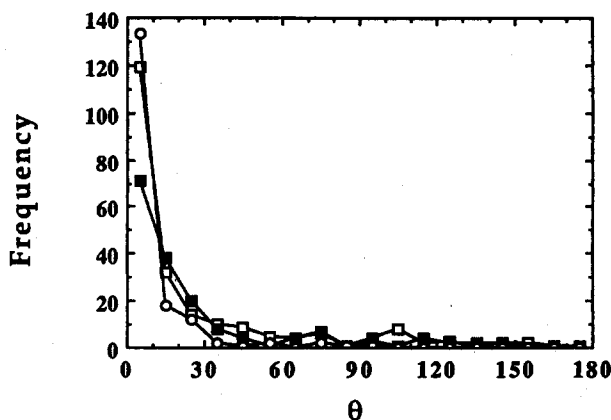


FIG. 4. Distribution of scattering angles for the nonreactive collisions. The symbols are the same as in Fig. 3.

ences when using any of the three-parameter sets. As an example, we compare in Fig. 5 the initial relative translational energy distribution with the one computed from the nonreactive trajectories corresponding to set 2. (Parameter sets 1 and 3 yield essentially identical results.) Note that in low-energy collisions the time scale for the molecule-cluster interaction is sufficiently long that the molecule rotates so as to find a favorable bonding orientation. Thus, one can easily rationalize the great disparity between the two curves in Fig. 5 at small values of the relative translational energy.

Interesting differences among the three sets of results also appear when one examines the structure of the clusters as manifested in the cluster compactness parameter γ discussed in the preceding section. Simulated annealing calculations on an isolated five-atom cluster yield the expected (on the basis of the work Halicioglu and White²⁸) trigonal bipyramid structure, which is characterized by a γ value [Eq. (2.4)] of 2.57. (A summary of the calculated γ is given in Table III.) The average γ calculated for the clusters prior to the collision of the CO molecule but subsequent to the initial short equilibration is only slightly larger, 2.60, and so one concludes that the 400 K thermal motion of the cluster atoms does not produce a significant perturbation of the structure. This latter value also characterizes the final state of the clusters in nonreactive trajectories. In all cases investigated here we find that the initial and final γ 's for trajectories which do not lead to addition of the CO agree with one another to within ± 0.01 , and therefore we can be fairly confident that any lack of agreement between initial and final values is indeed significant. Even for the equilibrium CO-Cu₅ structures there is an obvious difference between the structures obtained with the first two parameter sets and the one obtained with the third set. While sets 1 and 2 each yield γ values of 2.56 (note that this value is negligibly different from the one calculated in the absence of CO—the CO simply adds at one of the six threefold sites as depicted in Fig. 6), set 3 yields a γ of 3.37. So CO interactions described by the third parameter set produce a sizable distortion of the copper cluster geometry which tends to reduce all the C-Cu distances. The copper atoms tend to wrap themselves around the carbon atom somewhat, thereby reducing the

TABLE III. Metal cluster compactness parameters.

Parameter set	Z^*	$\gamma_{i(SA)}^a$	$\gamma_{b(SA)}^b$	γ_i^c	γ_b^d	γ_{nb}^e
1	0.400	2.57	2.56	2.60	2.69	2.61
2	0.300	2.51	2.50	2.53	2.62	2.54
2	0.400	2.57	2.56	2.60	2.84	2.60
2	0.500	3.56	3.55	3.57	3.54	3.56
3	0.400	2.57	3.37	2.60	3.04	2.61
3	0.500	3.56	3.46	3.57	3.43	3.58
4	0.400	2.57	2.59	2.60	3.45	2.58

^a From simulated annealing calculation on isolated Cu₅ cluster.

^b From simulated annealing calculation on CO-Cu₅.

^c From initial trajectory conditions for Cu₅.

^d From final conditions of bonding trajectories.

^e From final conditions of nonbonding trajectories.

compactness of the cluster. This effect is not so dramatic, however, in the average γ calculated from the copper atom positions at the end of the reactive trajectories. For these clusters we find a γ of 2.69 when using parameter set 1, a somewhat larger value of 2.84 when using set 2, and a still larger value of 3.04 when using set 3. Clearly, the collision, in general, leads to a distortion of the cluster, and the short time scale (< 10 ps) considered here is insufficient for the bound system to find its equilibrium structure. However, at longer times a comparison between experimental and theoretical estimates of the degree of copper cluster distortion should permit one, in principle, to make an intelligent choice among the various potential parametrizations. Additional experimental work which yields more structural data about the nascent clusters (infrared chemiluminescence measurements, perhaps) is urgently needed here.

Having compared three possible parametrizations of the forces between CO and the copper cluster, we can now make some general comments about the dynamics in this particular system. First, at 400 K CO is found to add readily to the metal cluster, yielding complexes which appear stable over the 10 ps trajectory time. (This last observation suggests an upper limit to the rate of unimolecular decomposition of the complexes in the absence of stabilizing third-body colli-

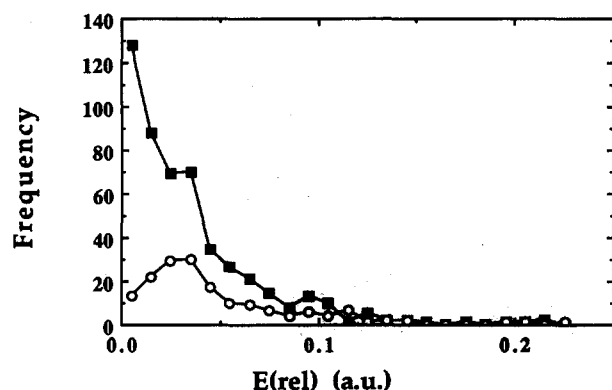


FIG. 5. Distribution of initial (solid squares) and final (open circles) CO-cluster relative translational energies for nonreactive collisions.

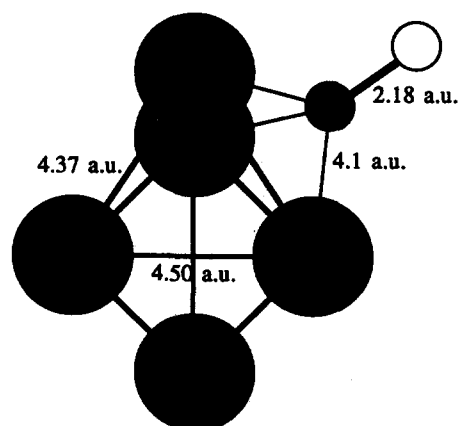


FIG. 6. Equilibrium CO-Cu₅ structure from a simulated annealing calculation using parameter set 2 and $Z^* = 0.400$. The atoms are depicted as in Fig. 1.

sions.) In particular, collisions at small impact parameters have a high probability of being reactive, although the exact degree of reactivity varies somewhat as the potential parameters are changed. Actually, given the paucity of hard information concerning the interactions in CO-Cu₅, it is encouraging that the gross differences in the results obtained with the various parametrizations are not greater. Second, as a consequence of the fact that most of the nonreactive collisions are associated with large impact parameters, the calculated final CO rotational distributions are strongly dominated by $\Delta J = 0$ and, as one should certainly expect at these temperatures, there are no vibrationally inelastic trajectories found. Third, those collisions which do not lead to reaction yield, for the most part, CO-Cu₅ clusters in which the C-O bond is vibrationally excited ($\nu_f = 1$). This excitation stems not from a flow of energy into the bond, but from the decrease in the frequency of the oscillation as a consequence of the change in the reduced mass of the oscillator upon attachment of the copper cluster to the carbon atom. But because the C-O bond does not couple efficiently to the other modes of the cluster due to the frequency mismatch, this excitation energy is redistributed so as to produce dissociation of the complex on our time scale. (We should note that set 3, since it gives a "softer" short-range repulsive interaction, is associated with a somewhat larger number of unexcited bound CO species.) Finally, the amount of energy deposited in rotation and translation of the CO-Cu₅ product is small, with the rotational energy generally being < 0.005 eV (and often much less than this) and the translational energy being < 0.01 eV. The great majority of the system energy appears as vibrational energy of the complex. Given this final distribution of the energy, we certainly cannot assert that the reaction products are absolutely stable, and thus a future focus of our work will be the assessment of cluster stability and the determination of lifetimes.

We also have sought to evaluate the importance of including internal motion of the cluster in these calculations by constructing trajectories in which no internal energy is deposited initially in the copper cluster. At time zero the clusters are found in their equilibrium structures, with the only positional randomization coming from a random rotation of the rigid body through three Euler angles.⁵⁶ These "cold cluster" results, obtained using parameter set 2, have turned out to be statistically indistinguishable from the corresponding 400 K cluster results (see Table II). At least for this set of assumed potential parameters, there seems to be no significant coupling between the vibrational degrees of freedom of the cluster and the molecule-cluster degrees of freedom on the time scale considered here. It should be noted that experiments which yield information about internal temperatures of reacting clusters as yet have not been reported.

As we mentioned above, we also have considered other values of the parameter Z^* which scales the contribution of three-body interactions to the cluster potential energy. One, for example, might choose a Z^* of 0.3 as did Erkoç and Katircioglu²⁷ in a study of gold microclusters and make the not unreasonable guess that this Z^* value is characteristic of elements of this group. The reactive cross section calculated

using parameter set 2 and $Z^* = 0.3$ is not, however, statistically different from the one computed with $Z^* = 0.4$ (again see Table II). The general trends seen for changes in the cluster compactness parameter as a result of CO chemisorption also are very similar for the two-cluster potential-energy descriptions. A decrease in the three-body potential contribution yields a slight contraction of the cluster (γ drops from 2.57 to 2.51 in the Cu₅ simulated annealing calculations and from 2.60 to 2.53 in an analysis of the initial cluster atom positions prior to collision with CO), and the clusters are a bit more resistant to deformation upon addition of the molecule (while for $Z^* = 0.4$, the average γ changes from 2.60 to 2.84 as a result of the collisions, for $Z^* = 0.3$ the average change is only from 2.53 to 2.62). Nonetheless, the clusters remain essentially fixed in their trigonal bipyramidal geometries, with the chemisorption occurring at one of the six triangular faces.

It is interesting to generalize this investigation somewhat and ask whether or not a similar result would be obtained if the initial cluster geometry were quite different. For example, there is evidence that Al₅ clusters are not three dimensional but rather trapezoidal, having the form of a "W" (C_{2v}; see Fig. 7).²⁶ The guidelines of Halicioglu and White²⁸ suggest that $Z^* = 0.5$ will yield just such a structure, and in fact this value for the three-body scaling parameter was used by Pettersson, Bauschlicher, and Halicioglu²⁶ as well as by Halicioglu and Pamuk²⁹ in previous studies of small aluminum clusters. The difference is immediately obvious in a simulated-annealing calculation of the compactness parameter, where now one obtains a γ value of 3.56 (The average γ for initial trajectory conditions is essentially identical; specifically, here $\gamma = 3.57$). The geometry difference is not, however, associated with a radical change in the cluster reactivity. By looking at Table II, one will find that the increase in the reactive cross section is only about 10% irrespective of whether CO-cluster parameter set 2 or 3 is used. Thus, we observe that in this case the cross section is relatively insensitive to what would appear to be a rather drastic change in the cluster geometry. On the other hand, one should be careful in characterizing the change in cluster geometry as being all that significant. In both the D_{3h} structure and the C_{2v} structure there are found six threefold binding sites of roughly equal size, and so the binding energetics actually are not very different in the two cases even though the effective dimensionality of the clusters is clearly different. (Changes in the cluster geometry which yield qualita-

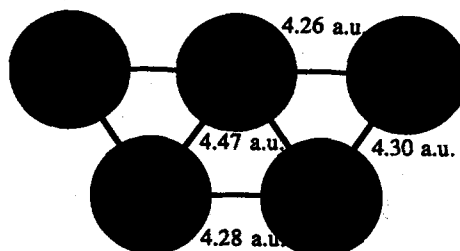


FIG. 7. Equilibrium Cu₅ structure from a simulated annealing calculation with $Z^* = 0.500$.

tively different molecule bonding environments might well be expected to exhibit more radical effects on the reactive cross section. For example, a large value of Z^* has been shown to yield a linear cluster having only twofold binding sites.²⁸⁾

We note that the C_{2v} cluster tends to become slightly more compact (if it changes at all) upon addition of the CO in contrast to the D_{3h} cluster's expansion under the same circumstances. The compactness parameters calculated using parameter set 4 via either simulated annealing or trajectories are nearly identical (3.46 and 3.43, respectively) and are less than the value calculated for free Cu_5 (3.56). Using set 3, one finds that all the γ values are the same within a reasonable estimate of the statistical error ($\gamma = 3.56 \pm 0.02$).

IV. EXTENSION TO MORE STRONGLY BOUND SYSTEMS: CO-Ni₅

As we have suggested above, we wish to extend this study somewhat beyond just the CO-Cu₅ system so as to obtain a better grasp of the general nature of molecule-metal cluster collisions. The CO-Cu₅ system actually represents an important limiting case, since the binding is weak as compared with that which is inferred for other systems, and the bonding in the CO molecule itself is only slightly perturbed by the presence of the cluster. Suppose one examines collisions which yield stronger molecule-cluster bonds. The system CO-Ni₅ was also examined by Cox *et al.*,⁴⁶ who found the reactivity of the nickel cluster to be more than double that of the copper one. Unfortunately, there is little potential-energy information available for the CO-Ni_x system, but perhaps Cu₅ and Ni₅ are not all that different. (We note, for example, that their ionization thresholds are nearly identical.^{44,57}) Therefore we have chosen, in the absence of other information, to model the forces in the Co-Ni₅ system using the same description that we have used for CO-Cu₅ (set 3) except that the carbon-nickel potential-well depth is taken to be twice that of the carbon-copper potential well. (The basing of this alteration on parameter set 3 has been done for convenience. Recall that with this set of parameters the overall molecule-cluster binding energy is determined almost exclusively by the magnitude of the individual carbon-metal atom bond energy.) Using this new set of potential parameters (set 4), we obtain a reactive cross section ($191 \pm 6 \text{ \AA}^2$) which is larger than those calculated for the systems with smaller molecule-cluster binding energies, but we do not find nearly as great an increase in the reactivity as was reported by Cox *et al.*⁴⁶ The doubling of the carbon-metal well depth while keeping other potential parameters the same here yields only about a 15% increase in the cross section.

Why is there such a difference in the behavior of the results of these calculations and the experimental ones for CO-Cu₅ and CO-Ni₅? First of all, it should be noted that while the experimental reactivity is clearly greater in the case of the nickel cluster, the reported error estimates in those experiments are large. A simple propagation of error calculation yields a reactivity ratio of Ni clusters to Cu clusters of 2.3 ± 1.7 , so too much faith cannot be placed in the precise

value measured for the ratio. Our calculated ratio of reactive cross sections obtained using sets 3 and 4 is 1.14 ± 0.05 , which indeed does fall within the large error bars of the experimental value. On the other hand, it is not clear that the simple potential modifications suggested here really represents a changeover from the CO-copper system to the CO-nickel system. Particularly in the limit of relatively weak bonding, it seems unlikely that the net molecule-cluster interaction would depend almost exclusively on the individual carbon-metal interactions as opposed to reflecting a compromise between the carbon-metal attractions and the oxygen-metal repulsions. Thus, it might be unrealistic to think that the comparison based on sets 3 and 4 is the appropriate one. Perhaps instead set 2 is the preferred description of the more weakly bound system. In that case, the ratio of cross sections increases to 1.43 ± 0.06 and a better agreement with the experimental number is obtained. The uncertainties noted here underscore the need for more work on the elucidation of the potential-energy functions for these systems.

We also have gone one step further and selectively increased the carbon-copper potential-well depth to its value in set 1. (This last set of parameters, set 5, is identical to sets 3 and 4 except for the value of D_{CCu} .) This increase yields a molecule-cluster binding energy which is essentially twice that obtained with set 4, but no statistically significant change in the reactive cross section. We offer the following explanation of this effect (or lack of an effect). In the case of the system described by a deep binding well, the incoming molecule experiences a large acceleration as it approaches the cluster, eventually slamming into the steep, repulsive potential wall. This collision, since it is very energetic and occurs on a very short time scale, cannot produce a transfer of much energy, so that a change in the potential-well depth at this point has but a negligible effect on the dynamics. This analysis is consistent with another observation made while generating the trajectories, namely that at the maximum trajectory time of 10 ps a large number of trajectories are characterized by molecule-cluster distances which are just short of the limit beyond which the system is judged not to be bound (10 Å here). In the process of analyzing the previous sets of trajectories, these particular trajectories were singled out and their time limits were increased to 20 ps, but no more than one trajectory of each set of 500 was found to describe a bound system at 10 ps but an unbound one at 20 ps. In contrast, the cross section calculated using set 5 and a maximum trajectory time of 15 ps is only 79% of the value obtained with a maximum trajectory time of 10 ps. [See Table II, specifically entries 5(a) and 5(b). The set of trajectories run to 15 ps was generated using a smaller time step, namely 2.0×10^{-4} ps, in order to retain comparable energy conservation.] An examination of the individual trajectories after the longer time period still reveals a large number of trajectories which appear as if they might lead to dissociation if only the time interval were extended for a picosecond or two more. Quite clearly, many of the collision complexes formed in this instance are metastable. If the collisional energy transfer is quite small when the binding well depth is large, then subsequent redistribution of the energy of the system may lead to dissociation of the complex. Third-body colli-

sions should therefore be of particular importance in stabilizing the strongly bound clusters at short times. The other cases considered here, in which the net binding energies are smaller, are associated with collisions which are more inelastic, so even though the potential wells are shallower, the systems fall farther into those wells. Third-body collisions would not significantly increase the stability of clusters interacting via these forces on the time scale considered in trajectory calculations.

V. CONCLUDING REMARKS

We have attempted here to elucidate some of the basic dynamical features of a particular molecule-cluster model system and to indicate a few generalizations applicable to other systems in which the molecule is nondissociatively chemisorbed.⁵⁸ In undertaking this project, we certainly acknowledge the fact that at best only sketchy data is available on the potential-energy surfaces for these systems. Consequently, a significant part of this work has involved an examination of several plausible potential-energy descriptions with an eye towards the identification of the dynamical differences among these descriptions. In comparing the results from these simulations with the reported experimental ones, we must interject a caveat, reminding the reader that two fundamental differences exist between the two approaches. First, the time scales are not the same; while trajectory calculations can be extended at most to a few tens of picoseconds, the experiments of Cox *et al.*⁴⁶ involve a time lag of 500 μ s between the reaction chamber and the detector. Thus, if unimolecular decay of the CO-Cu₅ cluster occurs on a time scale between these limits, the experimental results should show a decreased reactivity when compared with the present calculations. And second, we have not included the effects of third-body collisions with a buffer gas, collisions which could stabilize metastable collision complexes. Nonetheless, our calculations do reveal something about the nature of the nascent molecule-metal cluster, including the tendency of the metal cluster to distort upon addition of the CO. That sort of detail has not been available from the experiments which have appeared to date.

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