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We report an application of the semiclassical spectral intensity method to the calculation of the absorption spectrum of a simple molecular dimer, $(HCl)_2$, for both the free and physisorbed species. The calculated spectra show a clear indication of the presence of two distinct kinds of hydrogen atoms in this system, one which is involved in a hydrogen bond and one which is unaffected by the dimerization. We also find direct evidence that vibrational energy transfer plays an important role in the dynamics of this system and markedly affects the observed structure of the absorption spectrum.

I. INTRODUCTION

The burgeoning interest in dynamics at a fluid–solid interface stems primarily from a desire to exercise more control over heterogeneous catalytic processes. With the advent of ultrahigh vacuum techniques and the availability of a range of well-characterized laser sources, it is now possible to address many of the questions concerning adsorbate structure and dynamics that previously were only the subjects of spectulation. One of the more promising techniques for extracting information about such systems is infrared absorption–reflection spectroscopy (IRAS),[1] which in principle should yield much of the same sort of bond energy and structural data that can be derived from infrared studies of species in the gas or liquid phases.[2] We note, however, that while normal mode calculations have provided an important framework within which one may understand the results from these conventional fluid-phase measurements, theoretical models that yield simulated adsorbate spectra, and therefore aid in the interpretation of IRAS experiments, are not generally available. As a consequence of this shortage of theoretical techniques, it is not at all clear how one should proceed in quantitatively deconvoluting the wealth of information contained in the measured absorption peak shapes and positions.

In two earlier studies we described a semiclassical method for simulating infrared absorption line shapes that should provide just such a means for assessing the contributions of various dynamical influences to the observed spectral features.[3,4] That method, an adaptation of a formalism proposed by Marcus and co-workers,[5,6] involves the construction of the molecular dipole autocorrelation function, the Fourier transform of which yields the line shape function, on the basis of information gleaned from classical trajectories. The semiclassical component of the procedure enters in the selection of initial conditions for the trajectories, with there being a classical quantum correspondence principle which prescribes that initial classical action variables should be the arithmetic averages of the quantum numbers that index the initial and final states of the spectral transition.[7] We demonstrated in the first of our investigations that the methodology may be extended easily to the calculation of line shapes corresponding to individual vibration–rotation transitions and furthermore that this same technique may be used in the study of a simple physisorbed molecule.[3] Of particular interest was the observation that elastic rotational dephasing collisions are responsible for both a collapse of the rotational substructure and also line broadening at low initial rotational energies. On the other hand, high initial rotational energies were shown to give rise to a relatively unhindered planar rotation of the molecule. Since these initial results were obtained within a static-surface approximation, we then examined the changes in the calculated spectra arising when the thermal motion of the surface atoms was included in our model.[4] The net result of that inclusion was found to be best viewed in terms of an effective roughening of the surface, with the magnitude of the perturbation of the molecule's motion rising sharply at temperatures just below those at which significant thermal desorption occurs.

But even for certain simple physisorption systems, the analyses described in our previous studies will not be sufficient. In these systems the interactions between adsorbed molecules are sufficiently strong that any model which treats only isolated adsorbed species will be omitting a substantial fraction of the forces acting on the molecules. It is with this fact in mind that we began an investigation of the dynamics of an adsorbed dimer. Such a system does not provide, of course, a general model of an adsorbed molecule interacting with an arbitrary number of adsorbed neighbors nor does it represent a molecule that is part of an organized adsorbed cluster, but it does give us at least an initial glimpse at the dynamics in these larger assemblies. It should be noted that a study of this type is unique in that all the previous adsorbate dynamics studies of which we are aware have dealt with either isolated adsorbed molecules or monolayers, leaving untouched the consideration of the submonolayer coverage regime.

II. THEORY

It is well known that the power spectrum of a dynamical variable may be calculated by Fourier transforming the corresponding autocorrelation function. For the absorption of infrared radiation, one therefore has an expression for the line shape function $I(\omega)$ in terms of the (Heisenberg) dipole moment operator

$$I(\omega) = (2\pi)^{-1} \int_{-\infty}^{+\infty} dt \, \langle \mu(0) \cdot \mu(t) \rangle \, e^{-i\omega t}, \quad (2.1)$$

which is in fact no more than the standard first-order time-dependent perturbation theory result recast in the Heisenberg picture. With the equation in this form, it is easy to see that a transition from quantum to classical mechanics may be accomplished by replacing the time-dependent quantum operators by classical dipole moment functions. As in the past, however, we have found it more convenient to substitute for the rigorous definition of $I(\omega)$ given in Eq. (2.1) a simpler equation,

$$I(\omega) = (2\pi)^{-1} \lim_{T \to \infty} T^{-1} \left\langle \sum_{j=x,y,z} \left| \int_0^T dt \, \mu_j(t) e^{-i\omega t} \right|^2 \right\rangle, \quad (2.2)$$

that is identical with the previous result only in the long-time limit.[9] The advantage of this substitution, though, is that the problem is now cast in a form amenable to solution via fast Fourier transform techniques. [The actual evaluation of Eq. (2.2) has been carried out in a manner described previously,[3] which follows the method suggested by Wardlaw et al.[6]]

Although Eq. (2.2) has been evaluated by Berens and Wilson[10] using an ensemble of completely classical trajectories to which quantum corrections were subsequently applied, Marcus and co-workers have demonstrated that far fewer trajectories (in some cases as few as one) need be generated if one makes use of a quantum classical correspondence rule.[5,6] This rule, derived rigorously by Naccache[7] for a harmonic oscillator, predicts that the best aggreement between quantum transition moments and integrated classical intensities will be obtained when the initial classical action variables for the trajectories are taken to be the arithmetic averages of the quantum numbers that label the initial and final states involved in the spectral transition. The use of trajectories approximately quantized in this manner has been shown to yield good results both for simple model systems and also for systems of practical interest. For example, semiclassical dipole-moment matrix elements calculated by Stine and Noid[11] using the correspondence rule and a realistic diatomic potential function are found to be in excellent agreement with the corresponding quantum mechanical matrix elements. We also have had success in extending the formalism to the calculation of vibration–rotation intensities for free and physisorbed diatomics,[3] while Tully et al.[12] have obtained reasonably accurate values for the widths of lines in the infrared spectrum of a monolayer of hydrogen on a Si(100) surface. Jones et al.[13] also have applied the method recently to the study of the vibrational line shape of CO adsorbed on Pt(111).

III. SPECTRUM OF (HCl)₂

As a first step in the study of an adsorbed dimer, we have computed the spectrum of a gas-phase dimeric species, $(HCl)_2$. The potential energy functions adopted for this calculation were the hydrogen–chlorine Dunham oscillator diatomic potential proposed by Tipping and Ogilvie[14]

$$V(x_J, J) = hcB_e \gamma^{-2}(J) x_J^2 \left[1 + \sum_{i=1}^{5} a_i(J) x_J^i \right],$$

where x_J is a rotation-corrected reduced bond displacement [$x_J = (r - r_e)/r_e + $ "J corrections," $r_e = $ the HCl equilibrium bond length in the nonrotating molecule], and the C^* intermolecular potential of Klein and McDonald, comprising atom–atom potentials,

$$v_{HH}(r) = 9200 \exp(-2.725r),$$

$$v_{ClH}(r) = 2.05\{\exp[-4.8(r-2.56)]$$
$$- 2 \exp[-2.4(r-2.56)]\},$$

$$v_{ClCl}(r) = 32.6 \times 10^5 \exp(-3.8r) - f(r)(7.42 \times 10^3 r^{-6}$$
$$+ 5.56 \times 10^4 r^{-8} + 4.75 \times 10^5 r^{-10}),$$

$$f(r) = \exp[-(5.5-r)^2/r^2], \quad r > 5.5,$$

$$= 1, \quad r < 5.5$$

(all energies here being in kJ mol^{-1} and all distances in Å), as well as electrostatic potentials. These latter contributions are given by a distributed point charge model in which for each molecule a positive charge of magnitude 0.592 $|e|$ is placed on each of the atomic centers while a negative charge twice as great in magnitude is placed between the atoms at a distance of 0.455 Å from the chlorine atom. We have modified this model slightly, however, to take into account the time variation of the molecular bond length (the C^* model per se assumes that each HCl molecule is a rigid rotor). In our model the negative charge is still located along the bond axis but at a distance of $0.455r/r_e$ (r_e in Å here) from the chlorine atom, with this placement maintaining the relative distances between the negative charge and the two positive charges.

A dipole moment function describing an isolated HCl molecule has been reported by Ogilvie, Rodwell, and Tipping,[16] with this function being derived in part from analytical matrix elements calculated using the diatomic potential function indicated above. This is the same fit to the molecular dipole moment (a Padé approximant) that we have employed previously. To obtain the dipole moment of the dimer, we simply have taken the vector sum of the individual molecular dipoles, even though we recognize that this construction may not yield a particularly accurate value, since we are ignoring the polarization of the electron densities of the molecules resulting from their interaction. We nonetheless feel that our model yields a reasonable description of the time dependence of the total dipole moment even though its actual magnitude could be significantly in error; it is, of course, the time dependence that determines the absorption frequencies via Eq. (2.1) or (2.2).

Initial sets of coordinates for the atoms were obtained via a thermally biased random walk (Monte Carlo with Metropolis sampling[17]) of the two molecules with the diatomic bond lengths, for convenience, being held fixed. The temperature of the system was taken to be 50 K, since it was for this temperature that the corresponding adsorbate spectra were to be calculated. The initial atomic velocities included contributions both from molecular center-of-mass motion (the velocity components being chosen via a random sampling from the appropriate Boltzmann distribution) and from internal motion (total molecular vibrational and angular momenta were calculated from the selected values of the

classical action variables and apportioned between H and Cl on the basis of standard techniques[18]). In setting the initial energies, we considered each molecule to be independent (i.e., we ignored the perturbation resulting from the intermolecular forces), and so the initial action variables were those appropriate to an isolated-molecule Hamiltonian. We believe that this approximation is justifiable in light of the detailed investigation of a model system reported by Wardlaw et al.,[6] which indicated that the use of a zeroth-order Hamiltonian in determining initial conditions for mean action trajectories can produce a good agreement between the semiclassical and exact quantum mechanical intensity results, especially at low energies.

The trajectories, initialized in the above fashion, were integrated for 12.2865 ps with a step size of 0.0001 ps using the modified Verlet algorithm described by Swope et al.[19] Cartesian components of the total dipole moment were stored every 0.003 ps, so that at the end of the trajectory there were 4096 points available for inclusion in the fast Fourier transforms. The theoretical resolution of the spectra obtained in this manner is roughly 2.7 cm^{-1}.

In Fig. 1 we give the spectrum corresponding to $v = 0 \rightarrow 1$, $J = 0 \leftrightarrow 1$ transitions by both molecules. [As we noted previously,[3] both the $J = 0 \rightarrow 1$ and the $J = 1 \rightarrow 0$ transitions are modeled by taking the classical action variable J_c to be equal to 1/2. The spectrum of a single HCl molecule determined using this same choice of initial classical action variables consists of two peaks, namely $R(0)$ and $P(1)$, the widths of which are less than the theoretical resolution of the calculation. Computation of the dimer spectrum included an averaging over results from 98 individual trajectories.] One finds there a broad absorption peak having two prominent maxima, at (approximately) 2847 and 2884 cm^{-1}. We may now compare this result with the high-resolution difference-frequency laser results obtained by Ohashi and Pine.[20] They have reported two bands, one centered near 2880 cm^{-1} and the other near 2857 cm^{-1}, that they assign to two qualitatively different hydrogen stretching motions. The first of these, namely the higher frequency one, is associated with a normal mode of the dimer in which

the principal motion is the stretching of the "free" H–Cl bond. The second band, on the other hand, is associated with a normal mode that mainly consists of "bonded-H" stretching, which is the stretching of a hydrogen atom that is involved in a hydrogen bond and which is located (roughly) between the two chlorine atoms. Our calculations reproduce these experimental results reasonably well, given the fact that the intermolecular potential function that we are using was designed to give acceptable thermodynamic and structural data for *liquid* HCl.

Since our calculation is quasiclassical, we cannot reproduce one of the important features of the experimental (quantum) results, the appearance of additional spectral lines that arise from transitions between energy levels that are split as a consequence of tunneling. Not surprisingly the HCl dimer appears to be qualitatively similar to the HF dimer,[21] the spectroscopy of which can be explained if the exchange of the bound and free hydrogen atoms is treated as a barrier penetration. Ohashi and Pine[20] have proposed that the absorption found at 2857 cm^{-1} corresponds to a transition involving two of these split states (v_2^+), while a lower frequency absorption at 2839 cm^{-1} corresponds to a transition between the other pair of states (v_2^-). In the absence of tunneling (i.e., in our classical system), the absorption would be expected to occur at a frequency that is midway between the two experimental frequencies, at about 2848 cm^{-1}. Note that this frequency agrees very well with our calculated value of 2847 cm^{-1}.

IV. SPECTRUM OF (HCl)$_2$/Ar(111)

Extension of the aforementioned methodology to the calculation of adsorbate spectra, the principal focus of the present work, requires the specification of a surface model and the relevant interaction potentials. Here, as in our earlier work, we have adopted a template model of the solid, choosing parameters appropriate to an Ar(111) crystal face. Since the details of that model have been reported previously, we refer the reader to those papers.[3,4,21] The potential interaction responsible for adsorbate binding, i.e., the one acting between the adsorbed and surface atoms, is described by a sum of pairwise additive terms, each being of a truncated Lennard-Jones type.[23] Specification of the initial conditions for trajectories appropriate to the adsorbed dimer system has been accomplished via the same Monte Carlo procedure (save for the inclusion of the surface atoms and the additional potential contributions) that was mentioned above in the description of the gas-phase dimer.

As a point of reference, the spectrum of a single HCl molecule adsorbed on an Ar(111) crystal face at a temperature of 50 K is given in Fig. 2. The transition simulated in this calculation by means of semiclassical trajectories corresponds to $v = 0 \rightarrow 1$ and $J = 0 \leftrightarrow 1$ ($v_c = J_c = 1/2$). Note the presence of a single broadened peak appearing at the position where one would expect to find the (forbidden) Q branch for the isolated HCl molecule. This sort of structure suggests that rotational dephasing is the primary dynamical process operating in this system and is responsible both for the appearance of only a single peak and for the observed homogeneous line broadening (as we noted in the previous
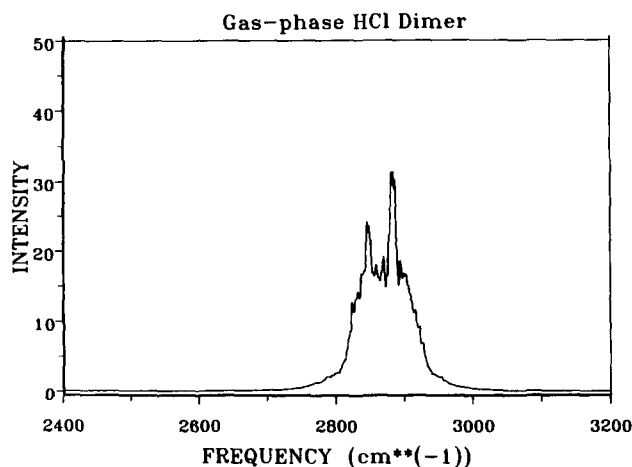

FIG. 1. Spectrum of gas-phase (HCl)$_2$ at 50 K, $v_c = J_c = 1/2$ for both molecules of the dimer. Ninety-eight trajectories are included in the calculation.

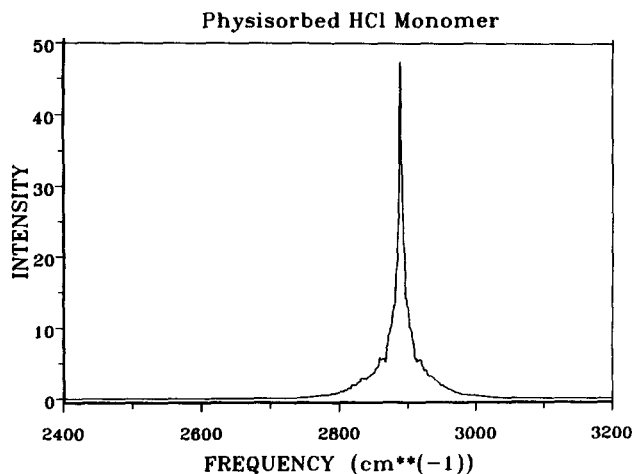Physisorbed HCl Monomer

FIG. 2. Spectrum of HCl/Ar(111) at 50 K, $v_c = J_c = 1/2$. 129 trajectories are included in the calculation.

Physisorbed HCl Dimer

FIG. 3. Spectra of $(HCl)_2$/Ar(111) at 50 K, $v_c = J_c = 1/2$ for both molecules of the dimer. In (a) surface atom dynamics are included, while in (b) a static-surface model is used. Ninety-nine trajectories are included in each calculation.

section, the isolated molecule spectrum for HCl determined from trajectories with the same initial conditions consists of a pair of very narrow peaks). If one were to omit surface atom motion (surface phonon modes) from the model, then the calculated peak would be found at the same frequency, but the peak width would be only about half of the corresponding value that we find in Fig. 2. As discussed in our previous work, the inclusion of surface atom motion produces an enhanced rate of dephasing attributable to an increase in the effective surface roughness and consequently an increase in the adsorbate linewidth.[4]

In Fig. 3 we give $v = 0 \rightarrow 1, J = 0 \leftrightarrow 1$ spectra calculated for the adsorbed HCl dimer, with both HCl molecules being excited. The upper panel (a) contains the result obtained when the full surface atom dynamics is included in the calculation, while the lower panel (b) shows the intensity pattern calculated when the surface atoms are held fixed in position. Note that the differences between the two spectra are sufficiently slight so as to be negligible; the dimer spectrum does not exhibit the line broadening which accompanies "turning on" the surface atoms that is characteristic of the monomer spectrum. This observation does not come as a great surprise, however, since the hydrogen bond between the HCl molecules is stronger than the molecule–surface bonds, and thus the intermolecular forces should be expected to dominate the dynamics. Due to the inconsequential effect of surface atom motion on the dimer spectrum observed here, we chose to carry out the remaining calculations within a static-surface approximation. The omission of surface motion greatly reduces the magnitude of the present calculation, with the number of first-order differential equations that must be integrated dropping, characteristically, from 168 to 24.

A comparison of Fig. 3 with Fig. 1 reveals that the basic structure of the infrared absorption spectrum of the HCl dimer does not change as a consequence of adsorption. In particular, the two peaks, corresponding to absorption by isolated dimer modes involving the vibrations of free and bonded hydrogens, appear at the same frequencies as do the two most intense features in the adsorbed dimer spectrum.
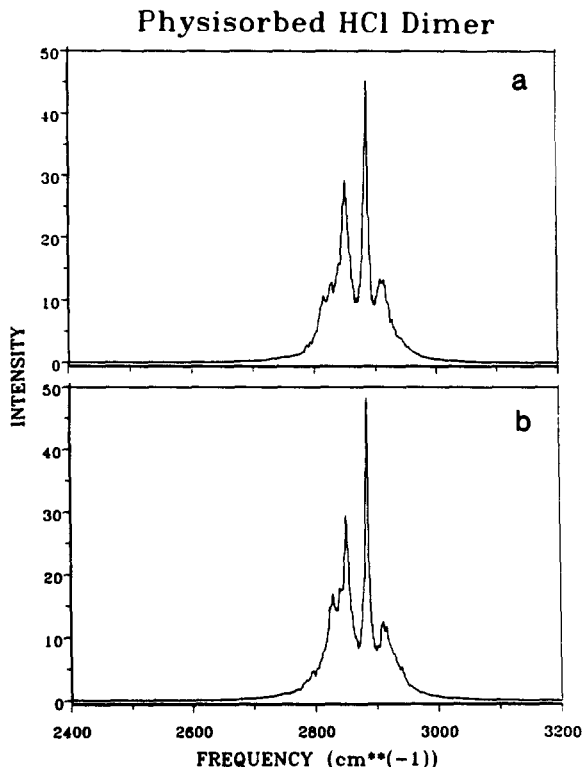
Greatly reduced, however, is the intensity between the principal peaks, so that the adsorbed dimer gives a cleaner, better resolved spectrum. In addition a relatively weak absorption on the high frequency side of the free H–Cl absorption (roughly 2910 cm^{-1}) is clearly evident.

Also of interest is the comparison of the spectrum calculated when both molecules of the dimer are excited with one deriving from an excitation of only one of these molecules (i.e., $v_c = J_c = 1/2$ for one molecule and $v_c = J_c = 0$ for the other). This latter spectrum can be seen in Fig. 4. Note here the relative decrease in intensity of the central peak. Of more
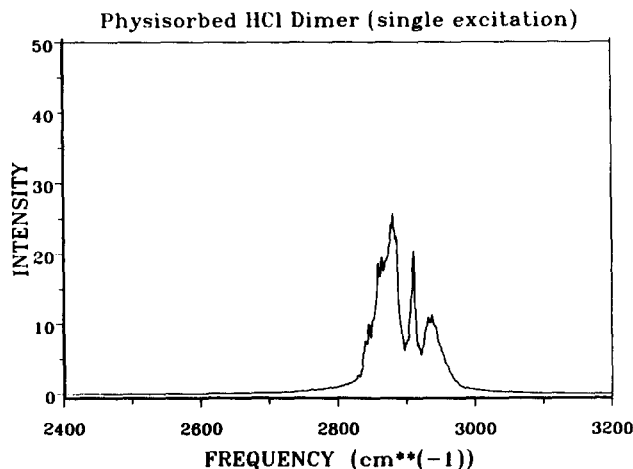
Physisorbed HCl Dimer (single excitation)

FIG. 4. Spectrum of $(HCl)_2$/Ar(111) at 50 K, $v_c = J_c = 1/2$ for one of the HCl molecules and $v_c = J_c = 0$ for the other.

significance, however, is the observation that the spectral peaks shown in Fig. 4 are shifted by an average of about 27 cm^{-1} to higher frequencies relative to those of Fig. 3. We believe this shift can be understood if one recognizes that as an HCl molecule is excited to higher and higher vibrational states, the observed infrared absorption frequency drops as an obvious consequence of the anharmonicity of the diatomic potential. Thus, a vibrationally excited molecule is not quite in resonance with one remaining in its ground state (and therefore oscillating with a higher frequency). The net result of this frequency difference is a blue shift of the dimer absorption.

Suppose, however, the frequency mismatch between the two molecules is much larger, a situation that would occur if a deuterium atom were substituted for one of the protium (^{1}H) atoms. The spectrum corresponding to this system (both molecules excited, $v_c = J_c = 1/2$) is given in Fig. 5, displaying the two sharp peaks that we would expect to see if noninteracting HCl and DCl molecules were adsorbed on the argon crystal face, even though a direct examination of the trajectories indicates that the dimers remain intact. If one is restricted to the study of actual molecules, then there is no intermediate case between $(HCl)_2$ and HCl–DCl that can be used to study the effect on the dimer spectrum of vibrational frequency differences between the molecules. But there is, of course, no limitation to particular mass values in a theoretical study, and so we have generated spectra for adsorbed dimers of the formula HCl–XCl, where the atom X is identical to a hydrogen atom except for its adjustable mass. If we take X to have a mass of 1.05 amu, then we obtain the spectrum shown in Fig. 6(a), which is similar in form to the $(HCl)_2$/Ar spectrum (Fig. 3) but is shifted by roughly 30 cm^{-1} to lower frequencies. An increase in the "hydrogen" mass yields a decrease in the frequency of the molecular oscillation and a slight frequency mismatch in the dimer. This case actually is very similar to the one discussed above in which only one molecule is excited, except for the fact that here the mismatch is towards lower frequencies and thus the shift is to the red. Larger frequency differences lead to more drastic alterations in the absorption spectrum. In
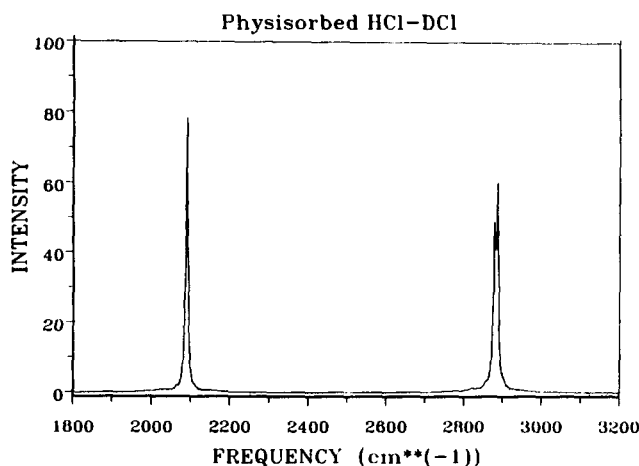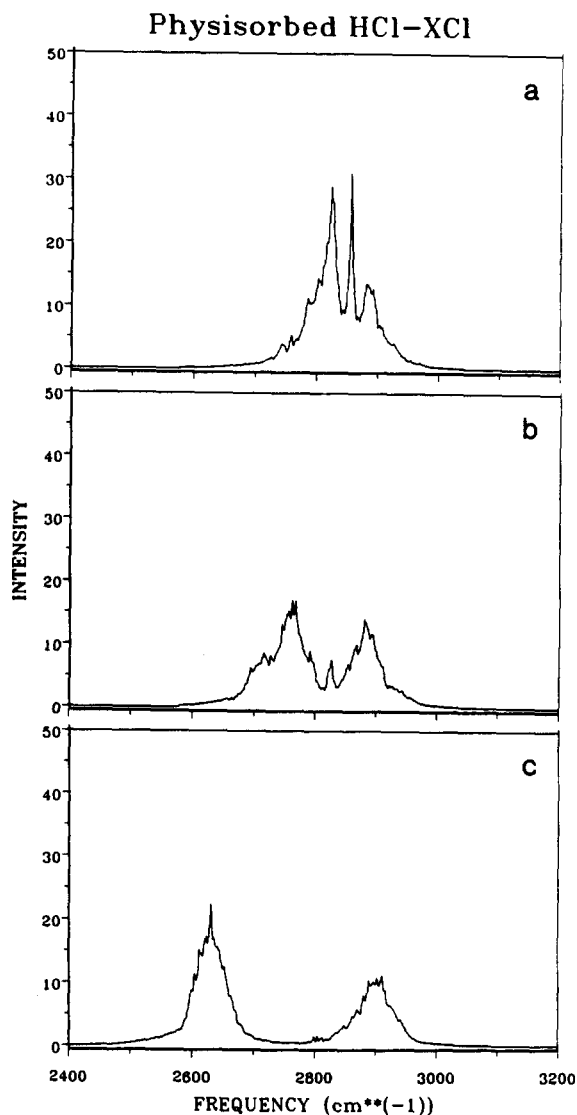

FIG. 6. Spectra of HCl–XCl/Ar(111) at 50 K, $v_c = J_c = 1/2$ for both molecules. (a) $m_X = 1.05$ amu, (b) $m_X = 1.1$ amu, and (c) $m_X = 1.2$ amu.

Figs. 6(b) and 6(c) we give the spectra calculated using X masses of 1.1 and 1.2 amu, respectively. Note that with an increase in the frequency gap between the two oscillators, the spectrum collapses to a pair of well-separated peaks, with further increases in the mass of X leading to a narrowing of these peaks and eventually to the spectrum of Fig. 5.

Having investigated the spectral manifestations of the dynamics of a simple adsorbed dimer, we moved to a more direct examination of the energy transfer in this system. These calculations involved trajectories initialized so as to correspond to particular quantum states (i.e., with integral values of the classical action variables) and consisted of generating the individual oscillator energies as a function of time. [Vibrational energies were calculated from the total energy by subtracting the individual molecular translational and rotational energies, the latter defined by expressions of the form $E_r = (r \times p)/2\mu r^2$, where r and p are the diatomic bond distance and relative momentum vectors.] In Fig. 7 we give some of the results from one of those trajectories, in particular the vibrational energies of dimeric HCl molecules

FIG. 5. Spectrum of HCl–DCl/Ar(111) at 50 K, $v_c = J_c = 1/2$ for both molecules of the dimer.
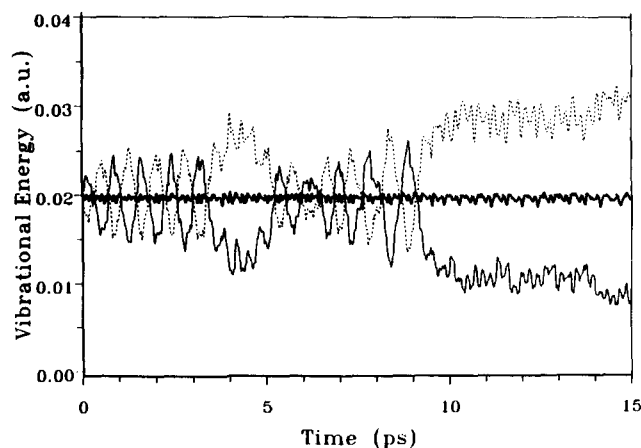
FIG. 7. Individual molecular vibrational energies (solid and broken lines) from one of the trajectories included in the calculation of the spectrum in Fig. 3(b). The heavy line across the center is the arithmetic average of the individual vibrational energies.
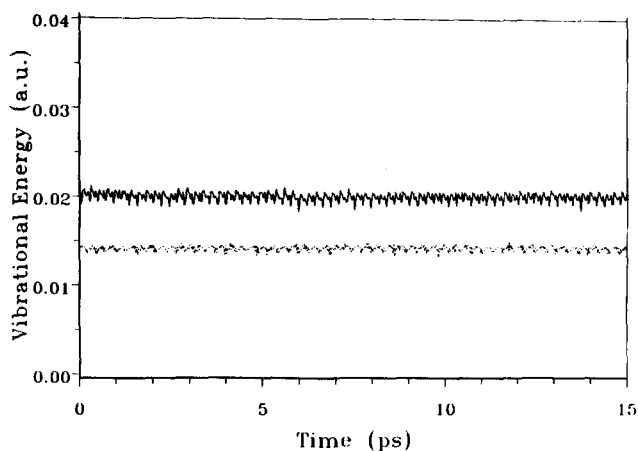
FIG. 8. Individual molecular vibrational energies for HCl (solid line) and DCl (broken line) from one of the trajectories included in the calculation of the spectrum in Fig. 5.

that at time zero were both characterized by classical action variables of $v_c = 1$, $J_c = 1$. One clearly sees there a beating back and forth of the vibrational energy between the resonant oscillators until eventually one of the oscillators has (approximately) two quanta of excitation and the other has only zero-point energy. The beat frequency corresponds to roughly 60 HCl oscillations per energy transfer cycle. [In the $(DCl)_2/Ar(111)$ system we find this frequency to be lower due to the lower DCl vibrational frequency, but it corresponds to the same number of oscillations per cycle.] There is, however, no net transfer of energy from the vibrational degrees of freedom to other motion (rotation or translation); the average vibrational energy (the heavy line in Fig. 7) is essentially constant in time even though the energies of the individual oscillators are not.

It is easy to understand why the energy beating does not continue indefinitely. Recall that due to anharmonicity the frequency of the HCl oscillation decreases as more energy is put into vibration. Therefore, if the vibrational energy should localize in one of the oscillators, the resulting frequency mismatch will tend to prevent the transfer back to the other oscillator. The driving force for this localization of the energy is the entropy, since there will be a net increase in the entropy of the system when the energy of one of the oscillators is minimized. In the present case this tendency towards energy localization will be enhanced when the energy is transferred to the oscillator containing the hydrogen-bonded atom, which is already at a lower frequency than is the oscillator containing the free hydrogen atom.

The plot shown in Fig. 7 should be compared with one depicting the results from an HCl–DCl/Ar(111) trajectory (see Fig. 8). (Recall that this system yields the spectrum given in Fig. 5, consisting of two sharp, well-separated peaks.) Here we find no evidence of a transfer of vibrational energy between these nonresonant oscillators or from molecular vibrational degrees of freedom to other degrees of freedom of the dimer. A similar result is found when equal amounts of vibrational energy are deposited in HCl and DCl (the $v = 2$ state of HCl is almost degenerate with the $v = 3$ state of DCl, but the plot of vibrational energy vs time shows no indication of energy exchange).

With the recognition that vibrational energy transfer plays an important role in the dynamics of the dimer, we are in a position to provide an explanation for a spectral feature about which we have until now reserved comment. That feature is the relatively weak but distinct high frequency absorption peak seen in the $(HCl)_2/Ar$ spectra [and, perhaps, in the free $(HCl)_2$ spectrum in Fig. 1, although it is obscured by the broad background absorption]. We attribute this peak to the presence of a high frequency oscillator, created when the initial excitation energy has localized itself in the other molecule of the dimer. Note that such a peak is also prominent in the spectrum of the dimer when only one of the HCl molecules is excited initially (Fig. 4). Is there a fairly simple way of testing the plausibility of this explanation? Suppose that in monitoring the system in which excitation energy is introduced into only one of the molecules (specifically, $v_c = J_c = 1/2$ for one of the molecules and $v_c = J_c = 0$ for the other), we accumulate values of the dipole moment of the excited molecule rather than the corresponding dimer dipole moment. If our interpretation of the spectrum is correct, then by ignoring the contribution of the unexcited, higher frequency oscillator we should remove the high frequency absorption peak. The power spectrum obtained by Fourier transforming the dipole moment of the excited molecule is shown in Fig. 9, with the most notable difference between this spectrum and the one of Fig. 4 being the near absence of a high frequency absorption. (A small residual peak may still be seen, though, as a consequence of the fact that our assignment of initial conditions based on uncoupled HCl oscillators is not quite correct.) We therefore feel confident in our assignment of the peak structure calculated for the $(HCl)_2/Ar$ system. These results, when taken together with the other observations noted above, clearly attest to the important contribution of intermolecular energy transfer to the dynamics of molecules adsorbed at finite coverages and to the importance of including such effects when analyzing the energy-loss spectra of these species.

Physisorbed HCl Dimer (single excitation, $\vec{\mu}_1$ only)
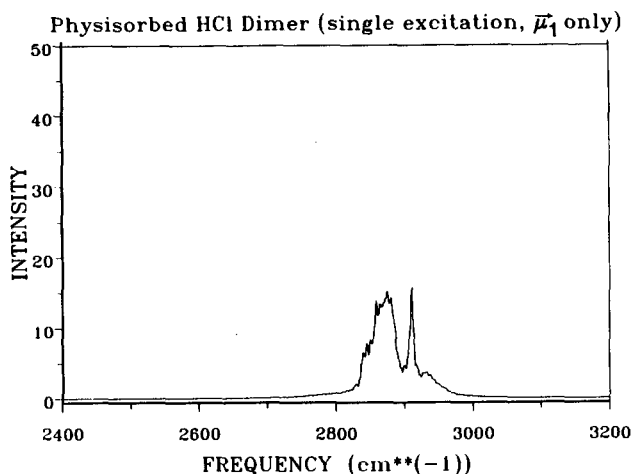

FIG. 9. Power spectrum derived from the same trajectories as the one in Fig. 4, but calculated by Fourier transforming only the dipole moment of the single excited molecule.

ACKNOWLEDGMENTS

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