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Cage effects and steric hindrance in van der Waals solids, with application to alkyl iodide photolysis in rare gas hosts

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Molecular luminescence in the near ir is produced by 259–290 nm pulsed “photodissociation” of CH_3I , CD_3I , and perfluoroalkyl iodide guests in rare gas hosts at 4.2°K. For CD_3I and CH_3I in Ne, the 15 member progression observed is assigned as fluorescence into high lying (near $v'' = 37$) vibrational states of the methyl-iodide stretch in the ground electronic state. Photoselection studies confirm the transition dipole lies along the methyl-iodine bond. The photodissociation cage effect is near complete, with only a minor quantum yield of permanent dissociation. Detailed analysis of the spectra suggests that the 0^+ “repulsive” excited state is actually slightly ($< 2000 \text{ cm}^{-1}$) chemically bound, and that the ground state potential is negligibly perturbed from its free molecule shape. A simple semiquantitative theory of the cage effect is proposed. In the impulsive limit, the excited state dynamics reflect a strong cage effect. However, in the adiabatic limit, the absorption and emission spectra reflect only a weak, van der Waals cage effect. The theory is applied to known examples of photodissociation in solids, and to rearrangements of larger molecules. A cage potential experiment of Schnepp and Dressler is reinterpreted.

I. INTRODUCTION

This paper is a study of alkyl iodide photophysics following ultraviolet “photodissociation” in van der Waals solids at 4.2°K. We have previously studied such a photodissociation “cage effect” involving a strongly predissociated (or avoided crossing type) excited electronic state in diatomic ICl .^{1,2} It was anticipated that the alkyl iodides would provide examples of a qualitatively different situation—solid state photodissociation on a purely repulsive potential having no bound levels in the gas phase. All alkyl iodides exhibit continuous 200–300 nm absorption interpreted as excitation of several repulsive states localized on the C–I bond.³ In the gas phase these states experimentally dissociate within essentially one vibrational period.^{4,5}

A population inversion on the spin-orbit transition $\text{I}^*(^2P_{1/2}) \rightarrow \text{I}(^2P_{3/2})$ is produced,⁶ thus indicating that the repulsive potential curve of the state principally responsible for the absorption correlates with alkyl radical + I^* . We conjectured that during photodissociation in the solid, the C–I bond length would increase until the repulsive cage forces on the alkyl radical and I^* equaled the repulsive chemical forces between the two fragments. A vibrationally relaxed, excited stationary state would then exist, which might subsequently be detected via fluorescence into the normal, chemically bonded ground electronic state. Analysis of such spectra would produce information concerning the host influence on the potential energy shapes in both excited and ground electronic states.

We in fact discovered that a molecular emission does accompany solid phase photodissociation of the perfluoroalkyl iodides.⁷ In this paper we observe that the corresponding emission from CD_3I and CH_3I in Ne and Ar shows resolved vibronic structure, and a detailed analysis is performed. Surprisingly, we find that the excited electronic state appears to be slightly ($< 2000 \text{ cm}^{-1}$) chemically bound in the isolated molecule. Ad-

ditionally, there is negligible change in the shape of the ground state potential, even for high lying C–I stretch levels close to the dissociation limit.

The specific excited electronic state we study is of current interest and practical importance in attempts to develop high power iodine atom 1.315 μ photodissociation lasers for laser-driven nuclear fusion applications.^{8,9} The fact that the excited state is slightly bound should influence the high pressure radical recombination kinetics, and thus power output, of these devices.

This photodissociation cage effect is part of a larger question concerning the role of steric hindrance in molecular rearrangements and chemical reactions in van der Waals solids. We propose a simple semiquantitative theory, showing that steric hindrance is only important on short time scales in the impulsive limit with respect to the elastic relaxation time of the host. These theoretical ideas are then applied to the known cases of the photodissociation cage effect, and to rearrangements of larger molecules such as stilbene.

II. EXPERIMENTAL AND OBSERVATIONS

The experimental apparatus has been previously described.² Briefly, we irradiate doped rare gas solids at 4.2°K with a frequency doubled, pulsed dye laser ($\Delta\lambda \approx 0.05 \text{ \AA}$, $\Delta t \approx 5 \text{ nsec}$). Time and wavelength resolved fluorescence is observed with a 1 m spectrometer and transient digitizer-signal averaging system.

We have previously reported the perfluoroalkyl iodide emission, which appears as a Franck-Condon envelope in the near ir.⁷ Individual vibronic bands are not observed. When CD_3I in Ne is irradiated near 2600 \AA , a long progression of about 15 broad bands with an average spacing of 279 cm^{-1} is observed as in Fig. 1a. Table I lists the positions of individual bands. This emission is independent of excitation wavelength in the range 2590–2700 \AA , and is vibrationally relaxed.

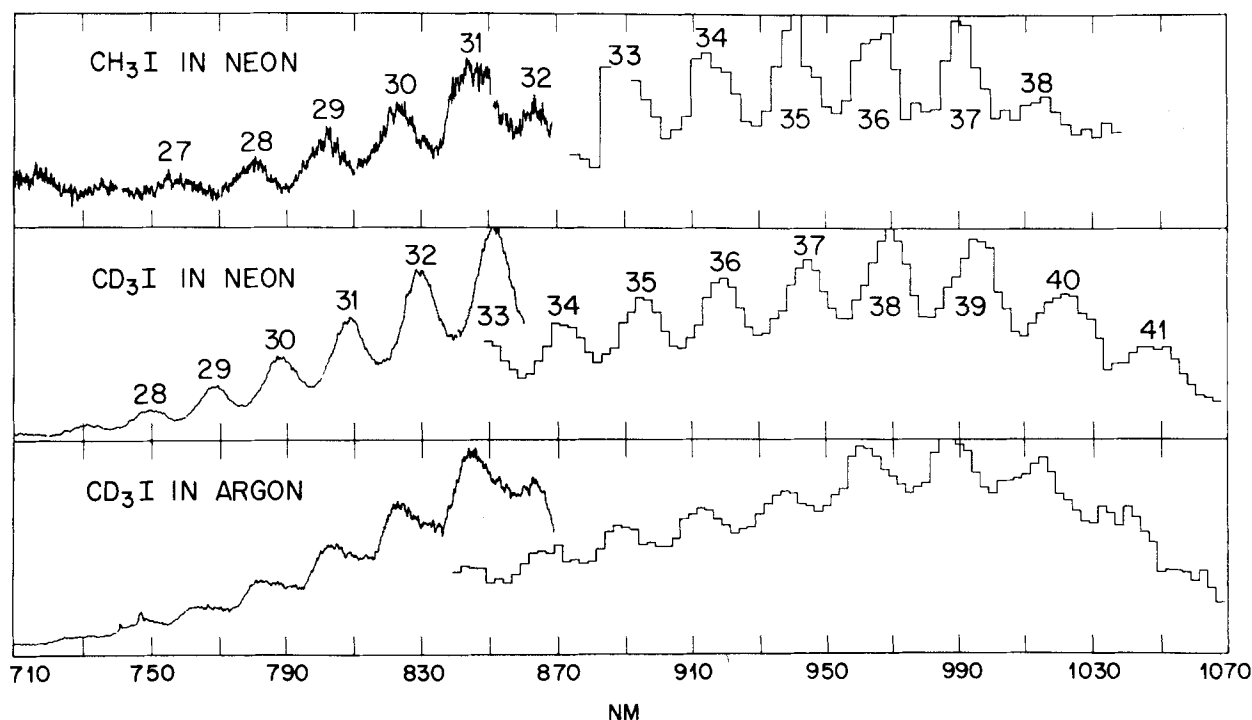


FIG. 1. Emission spectra at concentrations of 1:500 at 4.2°K. Resolution: 5 nm. The histograms plot the integrated emission intensity for three natural lifetimes in each case. Histograms taken with an S1 photomultiplier; continuous curves with a GaAs photomultiplier.

The normalized excitation spectrum shows no structure and peaks at 2610 ± 10 Å, in agreement with the gas phase absorption spectrum of CH_3I . In the case of CF_3I , the excitation spectrum peaks at 2670 ± 10 Å—again in agreement with the gas phase continuous absorption of CF_3I . Additionally, the lifetime is different for CD_3I and CH_3I , and still different for the perfluoroalkyls as previously reported. The emission intensity, which is proportional to the first power of laser intensity, decreases (“bleaches”) moderately as a function of irradiation time; it does not grow in as photoproduct emission does. These facts indicate the absorbing and fluorescing species is the parent alkyl iodide in each case.

A similar, yet slightly different and considerably weaker, emission is observed for CH_3I and appears in Fig. 1(b). The CD_3I lifetime is 25 nsec; the CH_3I lifetime is too short (< 5 nsec) to measure. We estimate from the relative emission yields that it probably lies below 1 nsec. The average band spacing in the CH_3I spectrum is ≈ 305 cm^{-1} ; in the CD_3I spectrum it is ≈ 297 cm^{-1} . This isotopic shift is consistent with assignment of the observed vibration to the methyl–iodine stretch.

The vibronic bands are broad with $\text{FWHM} \approx 150$ cm^{-1} ; apparently in the perfluoro compounds they are even broader, yielding spectra without resolvable vibronic structure. Normally, neutral molecules in rare gas hosts have inhomogeneous linewidths of only several cm^{-1} . Therefore, in the present case we conclude that the observed linewidth is homogeneous; individual vibronic transitions consist of a weak zero phonon line (ZPL) and a broad, intense phonon wing. The over-

lapping vibronic transitions apparently cover up the weak ZPL. The individual vibronic bandshapes do not appear to change across the Fig. 1 progressions.

We have recently shown that photoselection studies can be performed in rare gas solids.² These studies essentially determine the direction of the electronic transition dipole with respect to the molecular axes. If we consider CH_3I as a pseudodiatom, then the photoselection experiment theoretically yields $P(\equiv I_{\parallel}/I_{\perp}) = 3.0$ for a dipole along the C–I bond, and $P = 1.33$ for a dipole in the plane \perp to the C–I bond. Experimentally we measure $P \approx 1.8$ for CD_3I in Ne. We interpret this result as indicating the dipole is along the C–I bond, and that the theoretical value is lowered due to (a) light scattering in the optically inhomogeneous sample and/or (b) partial reorientation occurring accompanying the photodissociation–recombination process. Our interpretation of a transition dipole along the bond is entirely consistent with theory and gas phase photodissociation results.^{2–4}

TABLE I. Positions of the individual bands of Fig. 1 (cm^{-1}).

ν''	CH_3I	CD_3I	ν''	CH_3I	CD_3I
27	13 224	...	35	10 693	11 241
28	12 893	13 423	36	10 427	10 943
29	12 567	13 085	37	10 143	10 652
30	12 238	12 768	38	9867	10 376
31	11 919	12 445	39	...	10 103
32	11 606	12 128	40	...	9852
33	11 300	11 826	41	...	9602
34	11 001	11 534			

In general, the near ir molecular emission decreases as a function of time (bleaches) for continuous irradiation of a spot on the matrix. After short irradiation periods, the alkyl iodide emission is the only fluorescence (of $\tau > 10$ nsec) observed, but as the emission bleaches different band systems grow in with time. These new emissions must represent photoproduct luminescence accidentally excited by the laser. We have not investigated and assigned all the photoproduct emission; but in the case of parent CF_3I we have identified both IF fluorescence near 6000 Å and CF_2 ($^1B_1 \rightarrow ^1A_1$) emission¹⁰ in the 3000 Å region. Previous infrared¹¹ and ESR studies¹² of CF_3I photolysis in inert matrices have also detected CF_3 and CF radicals.

Detailed bleaching studies were carried out for CF_3I at 4.2 °K in Ne and Kr hosts. 1:5000 matrices of thickness such that the calculated optical density at 2680 Å was ≈ 0.03 for two passes of the laser beam through the matrix were used. For ultraviolet fluxes in the range $3 \times 10^{15} - 1 \times 10^{16}$ photons/cm² · pulse, the bleaching could be driven to completion ($I/I_0 < 0.05$). There was also no recovery of signal in Kr upon annealing of a bleached spot to 30 °K. Thus, the bleaching is effectively irreversible; there is no steady-state equilibrium between CF_3I and its photoproducts, and $kT \approx 20$ cm⁻¹ (30 °K) is not sufficient to thermally stimulate recombination.

The quantum yield Φ for bleaching per excitation is calculated from the light flux per pulse, the absorption coefficient, and the observed bleaching rate in units of number of pulses to reach $\ln I_0/I = 1$. The results are $\Phi \approx 2 \times 10^{-2}$ in Ne and $\Phi \approx 2 \times 10^{-3}$ in Kr for 2625 Å excitation. The principal uncertainty is the size of the focused laser spot (about 3×10^{-2} cm²), which is difficult to estimate because the laser operates with irregular and ill-defined transverse modes. Considering all the uncertainties, it is safe to conclude that these Φ 's are probably accurate to within an order of magnitude. We conclude that the permanent dissociation quantum yield is 10% or less and that there is a strong cage effect.

Experiments with a neutral density filter (OD=0.5) in the laser beam clearly show the bleaching rate is first order in laser power. Single photon dissociation into $\text{CF}_2 + \text{FI}$ is also energetically possible, but infrared experiments show that CF_3 is by far the major photolysis product. So it seems likely then that the dominant bleaching process is dissociation into $\text{CF}_3 + \text{I}$ in such a manner that recombination cannot be enhanced by $kT \approx 20$ cm⁻¹.

III. THEORY AND DISCUSSION

A. Emission spectroscopy

A detailed assignment and spectroscopic fit will yield the energy of the emitting vibronic state and the shape of the ground state potential curve. In particular, we want to know whether the emitting level lies above or below the gas phase $\text{CH}_3 + \text{I}^*$ dissociation limit, and whether the ground state potential is significantly changed in the solid from its gas phase shape.

Several methods may be used to determine the vi-

brational assignment. The analysis is hampered by our lack of knowledge of the $\text{CH}_3\text{--I}$ potential function. Only the lowest three levels, $v_3'' = 0, 1$, and 2 for the hydride, and two for the deuteride, are known experimentally from infrared spectroscopic studies.^{13,14} These infrared studies imply $\omega_3'' = 539.8$ cm⁻¹ and $x_{33}'' = 3.275$ cm⁻¹ for the hydride, and 507.3 and 2.89 cm⁻¹, respectively, for the deuteride. As the average spacing of the observed emission bands is 305.18 cm⁻¹ (297.67 cm⁻¹ for CD_3I), the assignment necessarily requires a long extrapolation.

The fact that the zero-phonon lines (ZPL) are not observed is a further source of uncertainty. For the purpose of data analysis, rather than to measure the positions of the broad and relatively flat maxima, we have used the sharply rising blue edge of each transition: The wavelengths given in Table I represent the half-height point of this blue edge. This blue edge, in addition to being better defined than the flat maximum, also more closely approximates the position of the ZPL. Our work on Cl_2 has shown that for high vibrational levels near a dissociation limit the shape of the phonon wings may vary¹⁵; however, this effect is not pronounced in our Fig. 1 spectra. The measurement of the phonon wing may, in addition to the random error caused by the lower accuracy of the wavelength determination for the broad wing, also include a small systematic error because of this effect.

Another source of uncertainty is the isotope effect. While for diatomic molecules simple and explicit formulas characterize the isotopic shifts, for a polyatomic molecule like CH_3I the isotopic shifts are more complex. That CH_3I cannot be treated as a diatomic is already evident from the infrared data. While for the diatomic molecule methyl iodide one would expect an isotopic ratio of $\rho = 0.923$ upon deuteration, the ir data show an experimental ratio of 0.940. The average spacing of the two progressions we observe shows a ρ of only 0.97. As one might expect for a molecule with many vibrational modes, the isotope effect changes as a function of vibrational excitation v_3'' .

We have attempted to fit simultaneously the measured bandheads of the two isotopic species in Ne to the spectroscopic constants ω_3 , x_{33} , and T_e using the diatomic isotopic relationships.¹⁶ The results are summarized in Table II. We carried out the fitting for various choices of the relative vibrational numbering and of the isotopic factor ρ . The constants and absolute vibrational numbering giving the best fit for each choice of ρ and of relative assignment are also shown in the

TABLE II. Results of the attempt to fit simultaneously the measured bandhead of the two isotopic species in Ne to spectroscopic constants using the diatomic isotopic relationship.

v''	$\Delta v''$	T_e	ω_3''	x_{33}''	ρ	RMS	D_e
12	0	17911	415	2.93	0.9405	58.9	9618
22	1	22706	493	3.25	0.9405	17.6	4823
37	2	30907	594	3.29	0.9405	18.0	-3378
26	1	24679	517	3.25	0.948	14.0	2850
27	1	25228	526	3.28	0.950	12.4	2301
29	1	26257	537	3.27	0.953	11.1	1272

table. Here the $\Delta v''$ in the second column gives the assignment of the first band of CD_3I at $13\,423\text{ cm}^{-1}$ relative to the nearest red shifted band of the hydride at $13\,224\text{ cm}^{-1}$; v'' gives the absolute numbering giving the best fit. The quality of each fit is judged by the mean square deviation of the observed and calculated band positions. The last column then shows the position of the emitting state with respect to the gas phase convergence limit at $27\,529\text{ cm}^{-1}$.¹⁷

The first three lines establish the relative vibrational numbering. All three use ρ of 0.9405 derived from the gas phase ir studies. $\Delta v'' = 0$ leads to an unrealistically low ν_3 of 350 cm^{-1} and also requires the emitting state to be bound by $\approx 10\,000\text{ cm}^{-1}$. $\Delta v'' = 2$ although it gives a better quality fit, leads to an extremely high ν_3 of 594 cm^{-1} , and also places the emitting level more than 3000 cm^{-1} above the gas phase dissociation energy—an unlikely result in the “adiabatic limit” (see following theoretical discussion). The third fit using $\Delta v'' = 1$ gives an acceptable value of ν_3 of 494 cm^{-1} and places the emitting level 4800 cm^{-1} below the convergence limit. The following lines then show the effect of variation of the isotopic ratio ρ . Decreasing this ratio (towards its experimental value) improves the quality of the fit, and also brings the value of ν_3 into closer agreement with the experimental value of 539 cm^{-1} . At the same time it reduces the bonding energy of the emitting state. In view of the uncertainties and the long extrapolation involved we cannot determine the position of the emitting level absolutely. Our best fits, however, indicate that the emitting state should

be bound by $\approx 1000\text{--}2000\text{ cm}^{-1}$. The ground state potential is also negligibly perturbed from a Morse potential based upon the known gas phase vibrational levels.

Figure 2 shows the Morse potential curve for the ground state of CH_3I and our best estimate for the potential function of the upper state. The experimental value of D_0 for CH_3I was used.¹⁷ The value of x_{33} we used was calculated from the experimental values of ν_3 and D_0 , using the Morse oscillator relations. The vibrational assignment shown in Fig. 2 was chosen because it extrapolates to the right value of ν_3 , using a reasonable value for the anharmonic term x_{33} and at the same time gives a reasonable fit of the two observed progressions. With this assignment one can note that the Franck-Condon maximum falls near $v'' = 36$ for the CH_3I and $v'' = 38$ for the deuterated species. A calculation of the classical turning points for the ground state potential function reveals that for $v'' = 36$ the outside turning point occurs near 3.32 \AA . This then should determine the position of the upper state potential minimum (considering the various uncertainties). The width of the Franck-Condon intensity distribution in the emission progression contains information about the upper state potential shape. In view of the uncertainties involved, a rigorous fitting of the Franck-Condon factors did not seem to be worthwhile. However, we have qualitatively compared the positions of the ground state outside turning points with the square of the upper state $v'' = 0$ wavefunction for various choices of the upper state vibrational frequency. The results indicate that $\nu'_3 = 150\text{ cm}^{-1}$ gives too narrow an intensity distribution; $\nu'_3 = 50\text{ cm}^{-1}$ suggests a distribution much broader than observed. The upper state vibrational frequency should therefore be near 100 cm^{-1} . The upper state Morse potential curve was therefore plotted with $\nu'_3 = 100\text{ cm}^{-1}$, $r'_e = 3.32\text{ \AA}$, and $D'_e = 1400\text{ cm}^{-1}$. It may be noted that this choice of the upper state parameters, which seem to provide the best agreement with our emission data, also places the ground state absorption maximum at the right wavelength near 2600 \AA .

Another consideration also suggests that the excited state we observe is chemically bound. The carbon atom hybridization changes from sp^3 to sp^2 as CH_3I photodissociates. If we were seeing fluorescence from planar methyl held against I^* , into the chemically bound ground electronic state of almost tetrahedral CH_3I , then the bending progression of CH_3 should also appear in the spectrum. It is not present, and we can only conclude that CH_3I has the same geometry in both electronic states we observe. The ground state vibrational levels we observe are bound by $0.5\text{--}0.8\text{ eV}$, and it seems reasonable that CH_3I is still tetrahedral in these states. It would be useful to have some independent evidence on this point. The current best interpretation is that CH_3I is almost tetrahedral in both electronic states.

B. Cage effect theory

We want to understand the cage effect on photodissociating molecules, and in general how the host hin-

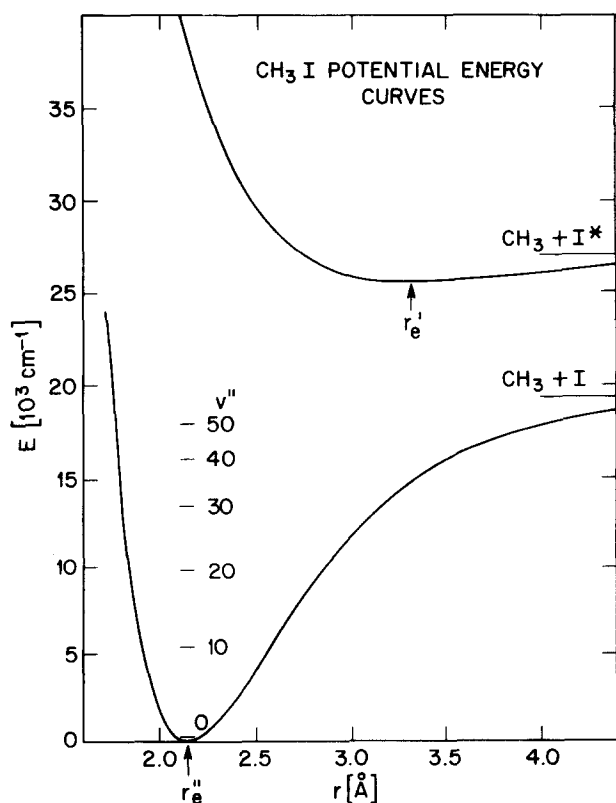


FIG. 2. Potential curves for upper and lower electronic states in the Fig. 1 emission spectra. See text for details.

ders rearrangements of polyatomic molecules. Let us first consider the energy required to expand the size of a vacancy in the solid; this energy must be provided by the guest molecule and is an intermolecular potential between guest and host.

First note that solid rare gases are extremely soft. The compressibility χ_s (inverse of the bulk modulus B) of solid Ne at 4.2 °K is 0.9×10^{-10} cm²/dyn¹⁸; this is an order of magnitude higher than such soft solids as Na metal or RbI crystal.¹⁹ This value is equal, within a factor of 2, to the compressibility of room temperature liquids such as ethanol.²⁰

For the moment let us assume that we can use a macroscopic theory to understand the expansion of a microscopic cavity. In classical continuum physics,¹⁹ the energy E required to compress a cubic crystal of initial volume V by ΔV is

$$E = \frac{1}{2} B \delta^2 V,$$

where $\delta \equiv \Delta V/V$. Physically it is assumed that the external pressure causing ΔV leads to a uniform adiabatic compression (increase in density) throughout the crystal. The time necessary to establish this new density is then the order of magnitude of the time necessary to propagate sound across the crystal.

Consider the following situation: One has a doped rare gas solid, and at $t=0$ pulsed excitation creates a density ρ of excited guest states such that the effective diameter of the molecule is doubled. The energy " e " required *per excited state* to double the radius of its cavity in the solid is then

$$e = \frac{1}{2} B \rho v^2,$$

where v is the volume increase of the site. e depends upon ρ because the effective volume of the host which can absorb the expansion of the guest is limited by how close the expanding cavities are to each other.

Suppose that v corresponds to a doubling of the diameter of a single vacancy in Ne, and that ρ corresponds to one excited state per 10^6 host molecules. Thus,

$$\rho = 3 \times 10^{16} \text{ per cm}^3,$$

$$v = 132 \text{ \AA}^3,$$

$$B = 1.1 \times 10^{10} \text{ dyn/cm}^2,$$

$$e = 2.9 \times 10^{-18} \text{ erg} = 0.015 \text{ cm}^{-1}.$$

A negligible amount of energy is required. This reflects the fact that in the normal spectroscopic case, when the excited states are far from each other, the 132 \AA^3 expansion can be taken up by a large volume of Ne. There is correspondingly a very small change in the average Ne internuclear distance, and as the host atoms are initially sitting at van der Waals minima where $dV/dr=0$, negligible energy is required.

Is this calculation really applicable to microscopic expansion around a guest molecule? As cavity expansion occurs, bonds between host atoms in a transverse direction to the direction of movement will tend to break and reform. This transverse bond breaking and

reforming may produce a series of activation energies, so that the expansion energy required will not be just a simple quadratic function of v . These activation energies may be several tens of cm⁻¹. It seems likely that the breaking and forming of transverse bonds will actually dominate the elastic compression energy calculated above; yet once these barriers are mounted (or tunneled through), negligible energy is still required.

We conclude there is only a minor van der Waals cage potential for host atom movement *in the adiabatic limit*, that is, in the limit of slow expansion such that the host has achieved a new state of nuclear positional equilibrium around the guest. In spectroscopic language, this particular vibronic transition is the zero phonon line (ZPL).²¹ No lattice phonons are created or absorbed because the lattice is produced directly in a new state of equilibrium. We specifically conclude that a guest molecular potential constructed from ZPL positions in an electronic transition will show only minor van der Waals-type changes from the same potential in the free molecule.

Consider now the relation between the Born-Oppenheimer approximation and the time scale of events. Molecules in rare gas solids normally exhibit a double Born-Oppenheimer approximation. There is the usual electronic-vibrational B-O separation, in which the guest electronic motion is faster than guest nuclear motion. One familiar result is that a Franck-Condon vibrational overlap principle controls the relative intensities of vibronic bands. Normally, internal guest vibrations occur at high frequencies with respect to lattice phonon frequencies, and there is a second B-O separation with host nuclear motion occurring on a time scale slow with respect to guest nuclear motion. Thus, a Franck-Condon host phonon wavefunction overlap principle controls the shapes of vibronic guest transitions. If there is no deformation of the host (i.e., the host nuclei equilibrium positions are the same in both states of the guest), then the ZPL is strong and the phonon wing is weak. The reverse is true if there is a substantial deformation. This second B-O separation is a necessary condition for a guest vibronic transition to be composed of a ZPL and a phonon wing²¹; if the guest frequency is similar to lattice frequencies, then a vibronic transition degenerates into a broad, featureless band.

Normally the change in the guest electronic wavefunction, and *not* the change in the bond lengths or angles, controls the host deformation. This fact is shown by the common observation that all bands in a given electronic transition have the same shape. The only known exception to this rule is the case of vibrational levels approaching a gas phase dissociation limit. In Cl₂, it is observed that as the dissociation limit is approached, intensity shifts from the ZPL into the phonon wing.¹⁵ This shows that the equilibrium positions of Ar atoms, in the Cl₂ excited state, are changing as a function of vibrational level. An important observation is that even in this case, the Cl₂ potential constructed from the ZPL positions shows negligible

(van der Waals) change from the gas phase potential. This confirms our assertion above that there is negligible cage effect potential in the adiabatic limit.

An experiment of Schnepf and Dressler appears to contradict this view.²² They observed the $(X-B)O_2$ absorption in rare gas solids, and constructed a potential from band maxima positions which is significantly steeper near the dissociation limit than the gas phase potential. They worked with limited spectroscopic resolution and did not notice the ZPL's; we suggest that in their spectra intensity is shifting from the ZPL into the phonon wing near the dissociation limit. Thus, their potential constructed from band maxima energies is not physically meaningful.

There is a strong cage effect, and steric hindrance does occur, in the impulsive limit for short times after excitation. The evidence is principally dynamical rather than spectroscopic; because as we have seen, if one has a molecular motion that is continuous (or weakly quantized) in the gas phase, then the corresponding solid phase spectrum is continuous without structure due to strong mixing between this motion and the host motions. In the photodissociation experiments for ICl and CH_3I , this impulsive limit produces a very fast vibrational relaxation of the kinetically excited photofragments. Because the diatomic dissociates fast with respect to the elastic relaxation time of the host, the fast fragments collide impulsively with individual atoms of the host (i.e., not with an infinitely massive host wall) and efficiently transfer kinetic energy. Permanent dissociation is prevented; however, if the separated fragments have activation energies for recombination, then they may be trapped as nearest neighbors after kinetic cooling to 4 °K.

It is useful to consider two cases where excited state dynamics indicates that steric hindrance does occur in van der Waals solids. The first is formation of intramolecular sandwich naphthalene excimers following excitation of dinaphthylpropane.²³ This excited state rearrangement occurs in fluid solutions, but not in low temperature glasses. The reason seems to be that the naphthalene excimer binding is short range in character and only occurs when the two rings have the correct sandwich conformation. In fluids, random thermal motion in the excited state accidentally brings the two groups into the correct conformation; in glasses there is no long range chemical attractive force to pull them together.

The second case is the triplet sensitized *cis-trans* isomerization of *trans*-stilbene, which again occurs in fluids but not in solids.^{24,25} This process is thought to occur via rotation of the two phenyl groups about the central C-C bond, which is principally a *single* bond in the lowest excited triplet. The triplet surface appears to be almost flat as a function of torsional angle; the torsional frequency has been estimated²⁵ to be of the order of 10 cm^{-1} . So again this appears to be a process caused by random thermal motion in the fluid.

Finally, consider the organic synthesis experiments of Chapman and co-workers in Ar lattices. These

workers have produced complex rearrangements of large polyatomics, apparently without a sign of steric hindrance. An example is the photochemical conversion of 2-pyrone to the bicyclic β -lactone, and ultimately to cyclobutadiene and carbon dioxide.²⁶ This again is consistent with our view that van der Waals hosts provide no hindrance to rearrangements driven by chemical forces.

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- ¹V. E. Bondybey and L. E. Brus, J. Chem. Phys. **62**, 620 (1975).
- ²V. E. Bondybey and L. E. Brus, J. Chem. Phys. **64**, 3724 (1976).
- ³A. Gedanken and M. D. Rowe, Chem. Phys. Lett. **34**, 39 (1975).
- ⁴M. Dzvoniak, S. Young, and R. Bersohn, J. Chem. Phys. **61**, 4408 (1975).
- ⁵S. J. Riley and K. R. Wilson, Discuss. Faraday Soc. **53**, 133 (1972).
- ⁶T. Donohue and J. R. Wiesenfeld, J. Chem. Phys. **63**, 3130 (1975).
- ⁷L. E. Brus and V. E. Bondybey, Chem. Phys. Lett. **36**, 252 (1975).
- ⁸F. T. Aldridge, IEEE J. Quantum Electron **1975**, 215.
- ⁹N. G. Basov, L. E. Golubev, V. S. Zuev, V. A. Katulin, V. N. Netemin, V. Yu. Nosach, and A. L. Petrov, Sov. J. Quantum Electron. **3**, 524 (1974).
- ¹⁰This system has been observed in absorption by A. Bass and D. E. Mann, J. Chem. Phys. **36**, 350 (1962).
- ¹¹D. E. Milligan, D. E. Mann, M. E. Jacox, and R. A. Mitsch, J. Chem. Phys. **41**, 1199 (1964).
- ¹²F. J. Adrian, E. L. Cochran, and V. A. Bowers, J. Chem. Phys. **43**, 462 (1965).
- ¹³E. W. Jones, R. J. L. Popplewell, and H. W. Thompson, Proc. R. Soc. London Ser. A **288**, 39 (1965).
- ¹⁴E. W. Jones and H. W. Thompson, Proc. R. Soc. London Ser. A **288**, 50 (1965).
- ¹⁵V. E. Bondybey and C. Fletcher, J. Chem. Phys. **64**, 3615 (1976).
- ¹⁶G. Herzberg, *Molecular Spectra* (Van Nostrand, Princeton, 1950), pp. 141-144.
- ¹⁷E. N. Okafo and E. Whittle, Int. J. Chem. Kinet. **8**, 273 (1975).
- ¹⁸E. I. Voitovich, A. M. Tolkachev, and V. G. Manghelii, J. Low Temp. Phys. **5**, 435 (1971). The compressibilities given by B. Meyer in *Low Temperature Spectroscopy* (Elsevier, New York, 1971), Table 8.6, have misplaced decimal points.
- ¹⁹C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1968), Chap. 4.
- ²⁰*Handbook of Chemistry and Physics* (Chemical Rubber, Cleveland, 1974), Table F-16.
- ²¹K. Rebane, *Impurity Spectra of Solids* (Plenum, New York, 1970).
- ²²O. Schnepf and K. Dressler, J. Chem. Phys. **42**, 2482 (1965).
- ²³E. A. Candross and C. J. Dempster, J. Am. Chem. Soc. **92**, 3586 (1970).
- ²⁴W. G. Herkstroeter and D. S. McClure, J. Am. Chem. Soc. **90**, 4522 (1968).
- ²⁵G. Orlandi and G. C. Marconi, Chem. Phys. **8**, 458 (1975).
- ²⁶O. L. Chapman, D. De La Cruz, R. Roth, and J. Pacansky, J. Am. Chem. Soc. **95**, 1337 (1973).