

cluster resulting from the absorption of a photon by a CS₂ molecule but whose nature is not otherwise defined; \mathcal{A}_i is a cluster, formed from the \mathcal{A} 's; it therefore involves i photons and i CS₂ molecules but its nature is also not further defined (e.g., it may be a cluster of i \mathcal{A} 's, of one \mathcal{A}_2 , and one \mathcal{A}_{i-2} , etc., or it may be a polymer molecule); and c is the number of photons and the number of CS₂ molecules involved in each nucleus. Note that these models only describe the dependencies of the nucleation rate on the CS₂ concentration and on light intensity but are not necessarily the actual elementary reaction mechanism.

Nucleation Decay Constant and Concentration Decay Constant. These decay constants are used to characterize the decay of the nucleation rate and the decay of the concentrations of \mathcal{A}_i after the UV light is blocked, respectively. The rate of nucleation, $J(t)$, observed after blocking the UV light is accurately approximated by an exponential decay, i.e.

$$J(t) = J_0 \exp(-\zeta t) \quad (\text{A-3})$$

where J_0 is the steady-state rate of nucleation and ζ is the nucleation decay constant. Similarly, the concentration decay constant η_i is defined by the equation

$$C_i(t) = C_{0i} \exp(-\eta_i t) \quad (\text{A-4})$$

where $C_i(t)$ is the concentration of \mathcal{A}_i and C_{0i} is a constant corresponding to a pseudo-steady-state concentration of \mathcal{A}_i .

References 25 and 35 provide details of how these decay constants are obtained. Furthermore, as has been shown,²⁵ a simple relationship exists amongst ζ and the η_i 's, i.e.

$$\zeta = \eta_i + \eta_{c-i} \quad \text{for } i = 1 \text{ to } c/2 \quad (\text{A-5})$$

Power Law Coefficients. Values of c , the number of photo-nucleators in each nucleus, are obtained by comparing the experimentally measured dependence of the steady-state rate of nucleation on light intensity with the dependence predicted by the model represented by eq A-2. These predictions were obtained by solving the resulting differential equations at steady state. However, to be able to solve the equations in closed form, reaction losses were neglected.¹¹ As a result, nonintegral values for c were obtained. For example, when nucleation is caused by clusters containing 7 \mathcal{A} 's, in the presence of 2 Torr of NO, the power law coefficient is 6.844. This difference increases as the ratio of second-order losses ($K_{ij}C_0^2X_iX_j$) to first-order losses (i.e., diffusion losses and quenching losses) increases. Thus, even if the reaction mechanism for photoinduced nucleation were exactly represented by eq A-2, power law coefficients obtained by equating c in eq A-1 to the measured light dependence are only lower bounds to the number of \mathcal{A} 's in each nucleus.

Registry No. CS₂, 75-15-0; H₃C(CH₂)₇CH₃, 111-84-2; H₃CCH₂OH, 64-17-5; 2-H₃CC₆H₄CH₃, 95-47-6; C₆H₅(CH₂)₃CH₃, 104-51-8; NO, 10102-43-9.

Molecular Beam-Laser Spectroscopy of the NeCl₂ van der Waals Molecule

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Laser-induced fluorescence excitation spectra for eleven bands of the B³Π_{0,u}←X¹Σ_g⁺ system of Cl₂ and the associated van der Waals molecule NeCl₂ have been obtained at 0.06-cm⁻¹ resolution in a free-jet expansion of Ne, Cl₂, and He. The observed rotational structure of the spectra of NeCl₂ is well simulated by a T-shaped, rigid Hamiltonian model for both the ground and excited states. The vibrational predissociation lifetimes ranged from 258 ± 42 ps for B(v'=9) to 33 ± 2 ps for B(v'=13). The intermode coupling and angular momentum effects were too small to be determined with the resolution achieved in this experiment.

Introduction

The study of the structure and dynamics of van der Waals molecules has become an active area for research in chemical physics. The triatomic van der Waals molecules, particularly those consisting of a rare gas atom bound to a diatomic halogen molecule, have been of both experimental and theoretical interest because their relative simplicity may allow a quantitative comparison between experiment and theory with few adjustable parameters. These triatomic complexes are easily formed in molecular beam expansions and may be probed spectroscopically by laser-induced fluorescence or by molecular beam resonance techniques. The van der Waals bond in the rare gas-halogen complex is very weak, less than the energy of a quantum of vibration of the halogen stretch for He and Ne compounds. Vibrational predissociation will occur if energy from the vibrational mode of the halogen molecule is transferred to the van der Waals mode. The vibrational predissociation process is thought to proceed

on a single adiabatic potential energy surface which makes the predissociation a theoretically accessible example of intramolecular vibrational relaxation (IVR).

The first studies of these molecules by Klemperer et al. involved detection of ArClF¹ and KrClF² by molecular beam resonance techniques. These ClF complexes have a linear geometry with the rare gas atom bound to the Cl atom. They rationalize the structure by considering the rare gas atom to be a Lewis acid which donates electrons into the halogen σ orbital which is the lowest unoccupied molecular orbital (LUMO) of the ClF. This model correctly predicts the linear geometry of the interhalogen van der Waals molecules, but fails to predict the geometries of the observed rare gas-homonuclear diatomic halogen complexes. These homonuclear halogen dimers are T-shaped, indicative of a van der Waals additive model of the binding. It is apparent that more experimental data are necessary for the development of appropriate theories to determine which is the most important interaction in the formation of the van der Waals bond.

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A detailed study probing the HeI₂ complex by laser-induced fluorescence was carried out by Levy and co-workers.³⁻⁶ The strong fluorescence of the B-X system of I₂ made possible the detection of both total laser-induced fluorescence and dispersed fluorescence. The van der Waals molecule HeI₂ was shown to be responsible for structural features appearing 3.4–4.0 cm⁻¹ to the blue of the (3–0) to (29–0) bandheads of free I₂.³ Analysis of the rotational band contours yielded a “T” shaped structure for the complex with a 4.5-Å He to I₂ center-of-mass distance. Homogeneous line widths were found to vary with the vibrational state excited, corresponding to predissociation lifetimes ranging from 220 ps for $v' = 12$ to 38 ps for $v' = 26$.⁴ The vibrational predissociation rates showed a quadratic plus linear dependence on the upper state vibrational quantum number. A study of the dispersed fluorescence spectrum of HeI₂ excited to the B(v') state showed that the fluorescence was dominated by I₂ in the B($v' = -1$) state.⁵ This led to a statement of the propensity rule $\Delta v = -1$ for this predissociative process.

The theoretical treatment of the vibrational predissociation in rare gas-halogen van der Waals complexes is based on the assumption that the normal vibration of the halogen molecule and the van der Waals stretching mode are only weakly coupled. Beswick and Jortner^{7,8} studied the vibrational predissociation of T-shaped complexes where the interaction between the diatomic halogen molecule and the rare gas atom was represented by a sum of Morse atom-atom potentials. The resulting close-coupling scattering equations could not be solved analytically, but numerical solutions gave vibrational predissociation rates from the widths of the resulting resonances. The model predicts that the predissociation rates have a strong inverse dependence on the energy difference between the initially bound complex and the final dissociated state. This “energy gap” model correctly describes the $\Delta v = -1$ propensity rule and the superlinear dependence of the rate on the vibrational quantum number but did not correctly predict the absolute predissociation rates observed in HeI₂. Also, the potential energy surface used by Beswick and Jortner has been shown to be quite unrealistic.⁹ Ewing has proposed a “momentum gap” model¹⁰ for vibrational predissociation which contains many features of the Beswick and Jortner analysis and also leads to a qualitative understanding for the basis of the momentum gap constraint on the V-T rate. In Ewing's model the V-T rate is limited by the ability of the internode perturbation part of the Hamiltonian to couple the nodeless $v = 0$ wave function of the van der Waals stretch to the oscillating plane wave that represents dissociated products. Since the plane wave frequency is proportional to the product momentum, higher momentum in the products leads to rapid dephasing of the coupling matrix element integrand and a slower V-T rate. For both the Ewing and the Beswick and Jortner models any rotational excitation of the dissociation products would serve to lower the momentum (or energy) gap and thereby increase the IVR rate.

Janda and co-workers have studied the van der Waals molecule NeBr₂ using laser-induced fluorescence techniques.^{11,12} Spectra were recorded at low resolution (0.1–0.2 cm⁻¹) for the van der Waals molecule associated with the (11–0) through the (30–0) B⁺ $\Pi_{u_g} \leftarrow X^1\Sigma_g^+$ transition of Br₂.¹¹ The NeBr₂ bands showed increasing spectral shifts of the complex from the free Br₂ with increasing v' , ranging from 5.5 to 8.8 cm⁻¹. The natural line widths

of the van der Waals features increased from the laser bandwidth limited value of 0.10 cm⁻¹ for NeBr₂ (16–0) to 3.1 cm⁻¹ for the (27–0) band, corresponding to vibrational predissociation lifetimes of 84 and 1.7 ps, respectively. They estimate the dissociation energy in the B state to be 64 ± 4 cm⁻¹ from the apparent closing of the one quantum predissociation channel near $v' = 27$. One transition, the B-X (10–0), was studied at high resolution.¹² The homogeneous line width was found to be 0.015 ± 0.005 cm⁻¹, giving an estimate of 350 ± 120 ps for the vibrational predissociation lifetime of $v' = 10$. This lifetime agrees well with an extrapolation of the low-resolution data. The data follow the trends predicted by the “gap” models discussed above.

Heaven and co-workers¹³ observed the van der Waals complex HeBr₂ using laser-induced fluorescence of the Br₂ B-X system at moderate resolution (0.05 cm⁻¹) in a free-jet expansion. Spectra were obtained for the (11–0) through (38–0) bands and rotational structure for several bands was resolved with analysis consistent with a T-shaped structure. The He to Br₂ center-of-mass distances are 3.7 and 3.8 Å in the ground and excited states, respectively. Lifetimes ranged from ≥ 100 to 1.8 ± 0.2 ps for the (12–0) and (38–0) bands of He⁷⁹Br₂, respectively. An upper limit of 23 cm⁻¹ for the He-Br₂ dissociation energy in the B state was provided by observation of rapid predissociation from the $v' = 40$ vibrational level. The lifetimes reported are again consistent with a simple “energy gap” model for vibrational predissociation.

The first laser-induced excitation study of a rare gas-interhalogen van der Waals complex was reported by Skene and Lester.¹⁴ A spectroscopic feature approximately 3.6 cm⁻¹ to the blue of the expected band origin of the ICl B($v' = 3$)-X($v'' = 0$) transition was attributed to HeICl. This is particularly interesting because no fluorescence from uncomplexed ICl was observed for this vibrational level because of subnanosecond electronic predissociation. This indicates that the vibrational predissociation of the He-ICl van der Waals bond is competitive with the electronic predissociation of the ICl molecule. Analysis yields a lower bound estimate of 550 ± 150 ps for the vibrational predissociation lifetime. Drobits et al.¹⁵ report the use of optical-optical double resonance techniques to study the dynamics of the vibrational predissociation process in the NeICl van der Waals complex. A pump laser excites the A-X transition, then at a time up to 15 ns later a probe laser scans through several E-A transitions of ICl while the fluorescence from the E state is collected. The lifetime for NeICl in the A state ($v_A = 14$) is 3 ± 2 ns based on experimental and theoretical ratios of the complex signal to free ICl as a function of time. The A state ($v_A = 14$) binding energy was determined to be 44 cm⁻¹.

Previously, we have studied the van der Waals complexes of Cl₂ with He¹⁶ and Ne.^{17,18} No lifetime information was obtained in the low-resolution (0.2 cm⁻¹) spectroscopy of the NeCl₂ complex. However, the observation of NeCl₂X($v'' = 1, 2$) in metastable vibrationally excited states was very interesting. The NeCl₂ exists for more than 10⁻⁵ s in the X($v'' = 1$) state even though the complex contains over five times the energy necessary to dissociate the van der Waals bond. High-resolution (0.01 cm⁻¹) spectra of the B-X (9–1) rovibronic bands of Cl₂ and the associated NeCl₂ van der Waals molecule were obtained. The experimental resolution was limited by lifetime and Doppler broadening, with analysis leading to an estimate of 258 ± 42 ps for the B($v' = 9$) state. The Ne to Cl₂ center-of-mass distance in the ground state, R_X , is 3.565 ± 0.035 Å based on the experimental line positions of two rotationally assigned, nearly unblended lines in the spectrum. The structure of both the HeCl₂ and NeCl₂ van der Waals complexes is T-shaped

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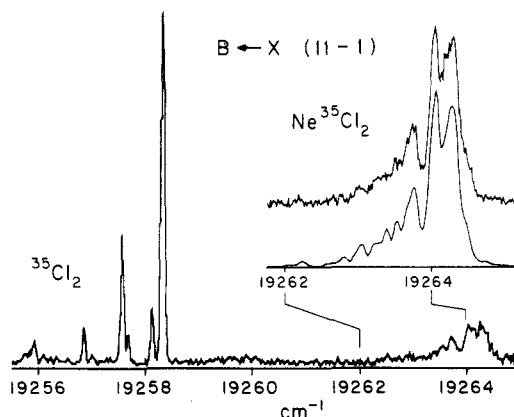


Figure 1. Laser-excited fluorescence spectrum of the B-X (11-1) vibronic band for Cl_2 and the associated van der Waals molecule NeCl_2 . The inset shows an expanded view of the transition for NeCl_2 with the fit to the data.

in both the ground and excited electronic states.

In this paper we report the dependence of the NeCl_2 B state lifetimes as a function of vibrational excitation. The observed trends are compared to HeCl_2 and to the energy gap and momentum gap laws. That the basic notion of energy gap laws applies to the rare gas-halogens seems to be beyond doubt. What remains is to obtain both potential energy surface parameters and predissociation rates as a function of vibrational and rotational quantum numbers which are accurate enough to test the details of presently available theory. Ideally, we want to have experimental measurements to evaluate the extent of coupling between the van der Waals and covalent bonds in these molecules. This would be measured as a change in the van der Waals bond length upon excitation of the halogen vibration. Also, we want to be able to measure lifetimes of individual rotational levels. In this paper we report progress toward meeting those goals via 0.06-cm^{-1} laser band width spectra of the NeCl_2 B-X, (7-0) to (13-0) and (9-1) to (12-1) vibronic bands. The spectra for the lowest excited electronic state vibrational levels show clearly resolved rotational transitions which can be used to extract the desired information. Analysis of this data shows that both the intermode coupling and the angular momentum effects on dynamics are quite small.

Experimental Section

The basic design of the molecular beam apparatus as used in these experiments has been described previously;¹⁷ therefore only a brief summary is given here. A supersonic beam was formed by passing a mixture of Ne and He at pressures varying from 100 to 300 psi over liquid Cl_2 at 200 K where the vapor pressure of Cl_2 is approximately 60 Torr. The mixture was expanded through a $35\text{-}\mu\text{m}$ pinhole into the vacuum chamber maintained below 10^{-4} Torr by a 10 000 L/s diffusion pump backed by a roots blower and mechanical pump.

Molecules were excited with a pulsed XeCl excimer laser (Lumonics 861-S) pumped dye laser equipped with an air-spaced Fabry-Perot etalon (Lambda Physik FL2002E). This dye laser is continuously tunable over a range of 20 cm^{-1} with a bandwidth of 0.05 cm^{-1} and a pulse energy of 1-3 mJ using Coumarin 503. The total fluorescence was detected by an S-20 photomultiplier and appropriate cutoff filters were used to reduce the stray laser light. The data were recorded on line by a multichannel signal averager connected to an IBM-PC microcomputer. The experiment consists of scanning the laser through a transition of Cl_2 and further to the blue while detecting the total fluorescence from the halogen and associated van der Waals molecules.

Results

The laser-induced fluorescence spectrum of the $^{35}\text{Cl}_2$ B-X (11-1) transition is shown in Figure 1. The feature observed $\sim 5.5\text{ cm}^{-1}$ to the blue of the $^{35}\text{Cl}_2$ band is attributed to the $\text{Ne}^{35}\text{Cl}_2$ van der Waals molecule on the basis of pressure dependence studies.^{17,18} The feature shows a nearly quadratic dependence upon backing

TABLE I: NeCl_2 Bond Lengths, Line Widths, and Lifetimes^a

band	$R_B, \text{\AA}$	Γ, cm^{-1}	τ, ps
7-0	3.52 ± 0.05		
8-0	3.51 ± 0.05		
9-0	3.53 ± 0.05	0.022 ± 0.003	240 ± 30
10-0	3.51 ± 0.05	0.029 ± 0.003	180 ± 20
11-0	3.51 ± 0.05	0.053 ± 0.003	100 ± 6
12-0	3.51 ± 0.05	0.081 ± 0.005	66 ± 4
13-0	3.55 ± 0.05	0.16 ± 0.01	33 ± 2
9-1	3.55 ± 0.04^b	0.021 ± 0.003^b	258 ± 42^b
10-1	3.54 ± 0.06		
11-1	3.51 ± 0.06	0.053 ± 0.003	100 ± 6
12-1	3.54 ± 0.06	0.070 ± 0.004	76 ± 4

$$R_X(v''=0) = 3.57 \pm 0.04$$

$$R_X(v''=1) = 3.53 \pm 0.04^b$$

^a In each case the rotational temperature used to fit the spectrum was $0.67 \pm 0.03\text{ K}$. ^b From ref 18.

pressure and disappears entirely in expansions consisting of only He and Cl_2 . Excitation spectra were obtained for the (7-0) through (13-0) and (9-1) through (12-1) bands of the B-X system of $^{35}\text{Cl}_2$ and the associated $\text{Ne}^{35}\text{Cl}_2$ van der Waals molecule.

The $^{35}\text{Cl}_2$ B-X excitation spectra were fit to a rigid rotor model, which included nuclear spin statistics. The temperature and the inhomogeneous line width were fit by a nonlinear least-squares routine while the rotational constants for both the ground and excited states and the band origin were held constant at the literature values.¹⁹ The Cl_2 transitions have inhomogeneous line widths of about 0.06 cm^{-1} which consist of a convolution of the laser bandwidth ($\sim 0.05\text{ cm}^{-1}$) with the Doppler width ($\sim 0.01\text{ cm}^{-1}$).

The NeCl_2 spectra were fit to a model consisting of a rigid T-shaped Hamiltonian for both the ground and excited states. The Cl-Cl bond distances, R_X and R_B , were assumed to be unchanged by the presence of the Ne and were held constant at the free Cl_2 literature values.¹⁹ The inhomogeneous line widths, with laser bandwidth and Doppler contribution, were held at the values obtained from fitting the spectra of uncomplexed $^{35}\text{Cl}_2$. From the high-resolution spectrum of the NeCl_2 B-X (9-1) transition previously reported¹⁸ we know that the portion of the spectrum which contains the most structural information is in the region to the red of the band origin. The portion of the spectrum to the blue of the band origin consists of a blend of many individual transitions and is less useful for extracting rotational constants. Since the (7-0) and (8-0) spectra were best resolved, they were fitted to obtain $R_X(v''=0) = 3.532 \pm 0.040\text{ \AA}$. This value was then used in fitting all other spectra originating at $v''=0$. $R_X(v''=1) = 3.536 \pm 0.035\text{ \AA}$ as previously determined¹⁸ was used in the fitting of each spectrum originating at $v''=1$. The fitted parameters were the rotational temperature, the natural line width, the band origin and $R_B(v')$. R , Γ , and τ are given in Table I. The quality of the fits is shown in Figures 2, 3, and 4.

The natural line widths for the (7-0) and (8-0) bands are too small to be determined from these spectra. For the other bands, the line width can be converted to a vibrational predissociation lifetime via the formula

$$\tau = (2\pi c \Gamma(\text{fwhm}))^{-1}$$

The effect of lifetime broadening is readily seen in Figures 3 and 4 as decreased resolution of the spectra. We are limited to estimating the vibrational predissociation rates for levels in the B state with $v' \leq 13$ because higher levels are dominated by electronic predissociation.²²

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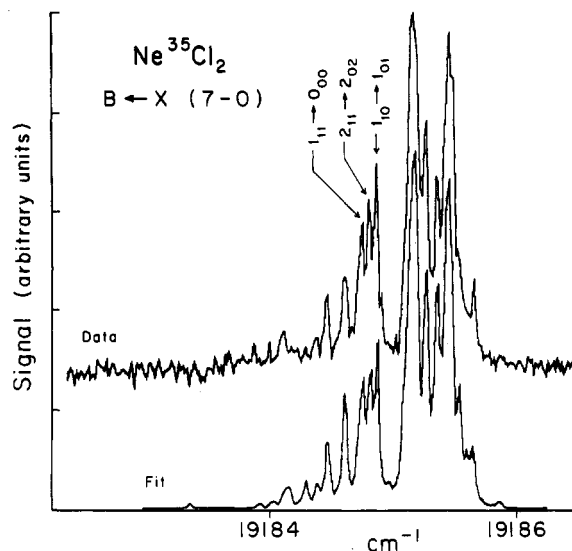


Figure 2. Laser-excited fluorescence spectrum of NeCl₂ associated with the B ← X (7-0) transition of Cl₂. The lower trace is the fit and the upper trace is the data. The labeled transitions give the $J_{K-1,K+1}$ rotational energy levels for the ground and excited states. The similar line widths demonstrate apparent independence of lifetime on rotational quantum number. See text for details.

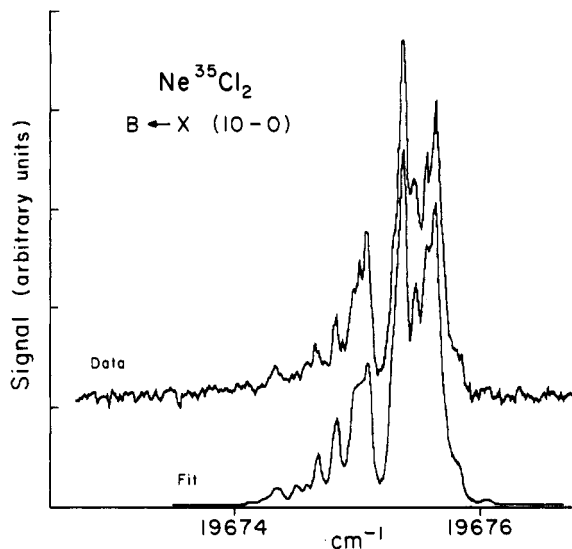


Figure 3. Laser-excited fluorescence spectrum of NeCl₂ associated with the B ← X (10-0) transition of Cl₂. The lower trace is the fit and the upper trace is the data.

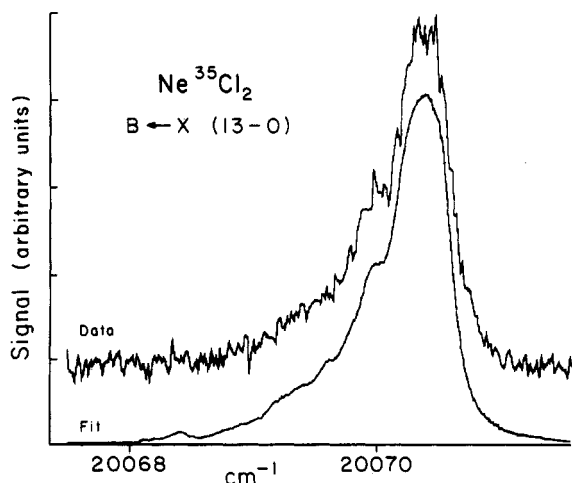


Figure 4. Laser-excited fluorescence spectrum of NeCl₂ associated with the B ← X (13-0) transition of Cl₂. The decreased rotational structure compared to Figures 2 and 3 is due to homogeneous lifetime broadening.

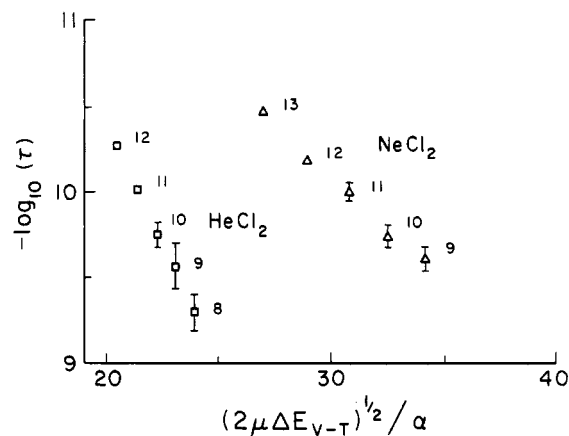


Figure 5. Plot of $-\log(\tau)$ vs. $(2\mu\Delta E_{v-T})^{1/2}/\alpha$ as a test of the momentum gap law for NeCl₂ and a comparison to HeCl₂.¹⁶ 95% confidence limits are shown. See text for details.

Discussion

The vibrational predissociation of rare gas-halogen dimers is particularly interesting because the combination of high-resolution spectroscopy and inelastic scattering data for the isolectronic series of molecules provides a more detailed test of IVR theories than for other classes of molecules. The dependence of the vibrational predissociation rate of NeCl₂ on the vibrational quantum number which we report here completes the matrix of possible combinations of He and Ne with Cl₂,^{17,18} Br₂,^{11,12} and I₂.³⁻⁶ We can now see how well the general trends predicted by "momentum gap" and "energy gap" models are obeyed by this group of molecules. The next phase of this project will be to make more quantitative predictions based on realistic intermode coupling parameters and understanding of angular momentum effects on the IVR dynamics. Analysis of the present data puts limits on the magnitude of these effects as discussed below.

Ewing's analysis¹⁰ of vibrational predissociation dynamics indicates that vibrational state lifetimes should be correlated by the formula

$$\log(\tau^{-1}) = b(2\mu\Delta E_{v-T})^{1/2}/\alpha h + c$$

where τ is the lifetime, $(2\mu\Delta E_{v-T})^{1/2}$ is the relative momentum of the dissociated products, and α is the Morse range parameter for the dimer bond. The constants b and c should be independent of the molecule at this level of approximation. Figure 5 shows how the NeCl₂ data reported here compares to the previously reported HeCl₂ data¹⁶ when correlated in this manner. D_0 for the complexes have been estimated by a one-dimensional zero point energy correction of the D_e values reported by Reid et al.²³ Values for the excited electronic state were obtained by subtracting the dimer band origin shift from the free halogen band origin.

As predicted by Ewing, the data for each molecule has a nearly linear dependence of $\log(\tau)$ on the momentum gap. Although the slopes of the two sets of data are somewhat different, this could be corrected by a slight adjustment of the Morse range parameters of the molecules. For a given momentum gap, however, the predissociation rates of NeCl₂ and HeCl₂ are different by several orders of magnitude. In fact, the lifetime is better correlated with the vibrational state quantum number than with the momentum gap.

By examining specific vibrational levels of I₂, Br₂, and Cl₂, we can compare the lifetimes of the Ne complexes of the halogens in states for which the product energy (and, less accurately, momentum) is nearly independent of which halogen is bonded to the Ne atom. For instance I₂, $v = 12$ has $\omega = 107$ cm⁻¹, Br₂, $v = 16$ has $\omega = 108$ cm⁻¹, while Cl₂, $v = 14$ has $\omega = 110$ cm⁻¹. The vibrational predissociation lifetimes for Ne bonded to each halogen in the stated vibrational levels are 229 ± 118 ,²⁴ 93 ± 10 ,²⁵

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and 30 ± 10 ps,²⁶ respectively. Thus when compared in this fashion the correlation of lifetime with the vibrational energy which might have been inferred from Figure 5 is no longer evident, even though the energy gap should be similar for the three molecules.

Several explanations for the deviations from simple gap law correlations of the data are possible. Most obviously, we have been treating the dissociation process as a simple, one-dimensional process. Not only does this ignore the role of angular momentum on the dissociation dynamics, but it also ignores the wide amplitude van der Waals motions within the molecules. In fact, for a rigid "T" shaped structure Ewing's analysis would predict that the dissociation rate would be zero;¹⁰ only deviations from that geometry allow the weak and strong bonds to couple. It is not hard, in principle, to see how to improve the models to account for both realistic potential energy surfaces and angular momentum effects. At this time, however, we have insufficient data to proceed with such corrections. The remainder of the discussion is intended to outline what data are needed and to illustrate the experiments necessary to obtain such data.

A fairly realistic representation of the NeCl_2 X state $v = 0$ potential energy surface can be obtained from the analysis of differential inelastic scattering data with constraints on the well position imposed by spectroscopy.²³ What remains is to determine the intermode coupling terms which relate the van der Waals bond to the Cl_2 covalent bond. One experimental source of such information would be to determine the dependence of the van der Waals bond length on the Cl_2 vibrational quantum number. As can be seen in Table I, such a dependence is too small to be measured with the present data which only determines R_X and R_B to 0.04 Å at best.

To estimate the extent to which this precision must be improved, consider the approximation that the Ne to Cl atom distance is independent of vibrational level. The increase in the Cl_2 bond length in going from the $v = 7$ level ($r_7 = 2.612$ Å)¹⁹ of the B state to the $v = 10$ level ($r_{10} = 2.722$ Å) would lead to a decrease of the van der Waals bond length of 0.02 Å between the two vibrational levels. Thus, to the extent that atom-atom properties determine the potential, modest improvements in the precision of rotational constant determination will start to provide the desired coupling information.

Another source of complexity in the vibrational predissociation is the effect of angular momentum. Angular momentum may help couple the IVR process via coriolis effects as have been postulated

for IVR in covalent molecules like formaldehyde.²¹ The present data show that angular momentum is not a dominating effect in determining the IVR rate for the NeCl_2 molecule. Each of the calculated spectra in Figures 2, 3, and 4 assumes that the natural line width is independent of J . If the line width were to increase as some strong function of J (i.e. J^2) one would expect the calculated spectrum to be too narrow for the lowest frequency transitions of Figures 2 and 3. The same J dependence would lead to a sharp, intense spike for the $J = 0$ line near the origin of Figure 4. Neither of these effects are observed in NeCl_2 or the other rare gas-halogens.

Finally, the deviation from simple "gap" laws which are observed may be due to rotational excitation of the halogen molecule during dissociation. Such rotational excitation, which might be considered more probable for the light halogens due to mass matching of the "half-collision" partners, would serve to lower the momentum gap and thereby also reduce the predissociation lifetime. Levy reported little rotational excitation of the I_2 upon dissociation of HeI_2 and ArI_2 .⁶ Preliminary measurements in our laboratory indicate slight rotational excitation of Br_2 upon dissociation of NeBr_2 . Such measurements have yet to be reported for NeCl_2 . Thus the role of product rotation remains open.

It is interesting to note that Drobits et al. observe substantial rotational excitation of the ICl product of vibrational predissociation of the NeICl A state $v = 14$ even though the lifetime is quite long, 3 ns.¹⁵ Unfortunately, little information is available on the potential energy surface of this molecule. It is obviously considerably more anisotropic than that of the homonuclear halogen dimers.

Summary

In this paper we reported the vibrational state dependence of the IVR rate for NeCl_2 in the B electronic state. Comparison of this data to the momentum gap law shows that while the law predicts the correct dependence of lifetime on vibrational level for individual rare gas-halogen molecules, the comparison of rates between molecules will require a more sophisticated analysis. The type of measurements necessary for more complete analysis have been discussed. Better measurements of high J line positions and lifetimes are necessary to obtain the intermode coupling terms in the potential energy surface and the angular momentum effects on the IVR rate. Product state measurements are necessary to determine the role of product angular momentum in lowering the momentum gap.

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(25) Unpublished data.

(26) The value given for Cl_2 $v = 14$ is extrapolated from the data in Table I. The extrapolation ignores the electronic predissociation which affects this level.