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Citation: *The Journal of Chemical Physics* **82**, 1298 (1985); doi: 10.1063/1.448452

View online: <http://dx.doi.org/10.1063/1.448452>

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Formation of a long-lived collision complex in alkali diatomic-rare gas collisions and rotational excitation via a mode-specific dissociation

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(Received 17 July 1984; accepted 24 August 1984)

We report an unusual pressure dependence of the gas phase dynamics of alkali diatomics in $^1\Pi$ excited states in their interactions with certain collision partners. This behavior consists of a change in the relative rates of the $\Delta J = +1$ and $\Delta J = -1$ collision-induced transitions, which results in a dominance of rotational excitation at high pressures. This effect occurs only for the e Λ -doublet component of the excited $^1\Pi$ state. Also observed is a change in the polarization of the parent line such that the polarization ratio increases with increasing pressure. The dependence of this behavior on intermolecular potential, reduced duration of collision, rotational state, and temperature lead us to propose that a long-lived complex or orbiting resonance is responsible for the effects observed. This species appears to be formed during the lifetime of the excited state of the diatomic. Knowledge of the molecule-fixed geometry of the Λ doublets allows us to propose a structure for the long-lived species and to speculate that the observed characteristic rotational excitation results from specific vibrational and rotational predissociation processes within the complex.

I. INTRODUCTION

There is considerable current interest in weakly or transiently bonded species and their consequences upon molecular dynamics both from an experimental and a theoretical point of view.¹ The spectroscopic studies of cooled van der Waals molecules by Smalley, Wharton, and Levy,^{1,2} Klemperer and co-workers³ have opened up new fields to the extent that there is now much experimental⁴ and theoretical⁵ interest in predissociation of weakly bound molecules and also in the influence of transient species on dissociation dynamics and other intermolecular events. Despite the relative weakness of the forces binding atoms or molecules together in this manner, the effects upon bulk properties of matter can be quite marked even at temperatures well above those at which the bound species are stable. Relatively little experimental data is available on the quantum resolved dynamics of weakly bound molecules in the high temperature, high pressure regime where the effects on bulk properties and, in particular, the onset of irregular behavior may be observed. There is also considerable interest in the product distribution of dissociation processes in weakly bound molecules since they provide a valuable test of theories of photodissociation.

In this paper we describe the observation of weakly bound rare gas-alkali dimer complexes formed from excited Π -state alkali diatomic molecules. Further, we have observed the product state distribution of the dissociation of the species and find the predominant decay mode to be a rotational excitation and Λ -doublet surface crossing. Here we refer to the species formed as a long-lived complex or orbiting resonance although alternative terminology for these transient molecules include collision complex, quasi-bound, or compound state. The analogy to the triatomic van der Waals molecules is strong and forms the basis of our discussion of the dissociation dynamics.

Much is known about the dissociation of rare gas atoms

bonded to diatomic molecules such as molecular iodine through the very thorough studies of Levy² and other workers.⁴ Two distinctive quantum features have emerged from the I_2 -rare gas work,² namely the variation of the rate of dissociation as a function of I-I stretch vibrational quantum and the observation of a $\Delta v = -1$ propensity for vibrational predissociation. Both observations have received theoretical justification through the work of Beswick and Jortner for the linear⁷ and the T-shaped⁸ geometries. Up until now only vibrational state product distributions have been measurable due mainly to the weakness of the signal and, in the case of the I_2 -rare gas complexes, the low value of the rotational constant. The partitioning of dissociation products into rotational quantum levels has not been determined despite the fact that any observed rotational propensities would be of considerable interest.⁶ In this work we present data which gives evidence of strong rotational selectivity in the dissociation products of a rare-gas alkali diatomic long-lived complex. The observation is not of an isolated, cooled and fully characterized species since the species are formed in thermal cells at elevated temperatures and with moderate pressures of rare gas atoms. Despite this the rotational propensities are very clear cut and the unique character of the excited Π electronic states of the alkali diatomics which are characterized by separate and nondegenerate electronic functions defined in the molecule-fixed frame, permits a molecular level interpretation of the dissociation process. It is of interest to note that the onset of the effects described (and hence formation of the long-lived species) occurs at quite modest pressures and thus we anticipate a very profound influence on the dynamics of rarefied gases which will undoubtedly affect bulk gas phase behavior. For this reason we feel that the effects described herein merit close study and we divide this paper into two main sections. In the first of these we concentrate on the evidence for the formation of the long-lived species in the cell. In the second we discuss the dynamical processes which might lead to the observed rota-

tional excitation and Λ -doublet surface crossing in the dissociation products.

II. EXPERIMENTAL

The techniques employed to measure fully resolved emission intensities and polarizations from laser-excited diatomic molecules have been described by us in previous publications.⁹ In this work, the Π states of Na₂, NaK, and NaLi were excited into specific rotational levels using the discrete lines of a 4 W argon ion laser. In fact, the line width of the laser was such (~ 5 GHz) that on several occasions, more than one rotational level was populated and when the separate series could be fully resolved, this afforded a means to examine the collision dynamics as a function of initial rotational state. In the case of coexcitation of this kind, care was taken to choose for examination spectral features which were not overlapped by other series. This did not in general present a problem.

The spectrometer used in this work was a Coderg PH1 double grating monochromator having a spectral resolution of 0.5 cm^{-1} . This was found to be adequate for the studies made here. Fluorescence was detected by an EMI 9658B photomultiplier tube and the signal processed in the manner described in earlier work.⁹ The sample cell was a 40 cm length thin-walled stainless steel tube having collars fitted at each end to hold optical windows which were held in place by Vitron O-rings. The center of the cell was heated by Kanthal wire windings embedded in ceramic cement and surrounding the tube. Inside the center of the tube was a stainless steel gauze wick to provide a large surface area over which the metals could run. At the temperatures and pressures we have employed it was found that the cell did *not* operate as a heat pipe oven.¹⁰ This is advantageous for the study of collision dynamics of alkali diatomics with foreign gases and the cell could operate for many hours without loss of signal.

Foreign gases were admitted to the cell via a side arm connected to a vacuum system. Pressure measurements were made using diaphragm and other gauges which could cover pressures up to a maximum of 120 mbar. Gases used in this work were added via reduction and needle valves from lecture bottles supplied by BDH Ltd. Typical purities were He 99.995%, Ar 99.99%. In the case of Na₂, sodium metal was introduced into the cell in small quantities under argon. For the work with NaK, a separate cell was used and it was found that the best results were obtained with a large excess of potassium over sodium. For the work with NaLi, approximately equimolar amounts of the constituent alkalis were used. Temperatures were measured using a thermocouple embedded in the ceramic cement in contact with the center of the stainless steel tube.

III. DISCUSSION

A. Identification of Resonances

1. Λ doubling in $^1\Pi$ state diatomics

The evidence for the existence of long-lived complexes relies upon a fully resolved spectroscopic study of the excited Π state of alkali diatomics and focuses in particular on the

relative probabilities of the collision induced Λ -doublet surface crossing rotational transitions. These are generally measured from the intensities of the Q_{+1} and Q_{-1} emission lines. Since the argument relies heavily on the $\Delta J = \pm 1$ relative transition propensities, we give first a brief discussion on the background and on the interesting history of the so-called “propensity rules” which have been the topic of much discussion in the past few years.

The Born–Oppenheimer wave functions for a Hund’s case (a) diatomic molecule in a $^1\Pi$ state such as Na₂, NaK, or NaLi can be written in terms of rotational and vibronic components

$$|JM\Omega^1\Pi vAS\Sigma\rangle = |JM\Omega\rangle |^1\Pi vAS\Sigma\rangle. \quad (1)$$

Here J is the total (rotational + electronic) angular momentum quantum number, S is the spin angular momentum, Λ , Σ , and Ω are the projections along the bond axis of the orbital, spin, and total angular momenta, M is the projection of J along the space-fixed z axis and v is the vibrational quantum number. For a $^1\Pi$ state, $S = \Sigma = 0$ and so $\Lambda = \Omega = \pm 1$. The $\Lambda = +1$ and $\Lambda = -1$ states in Eq. (1) are degenerate to first order but this degeneracy is lifted by perturbations from other electronic states.¹¹ The $^1\Pi$ energy levels therefore occur in closely spaced pairs which are termed Λ doublets. The Λ doublet wave functions are formed from linear combinations of the above states in order to be eigenfunctions of the parity operator \hat{i}

$$|JM\epsilon\rangle = \frac{1}{\sqrt{2}}[|JM\bar{\Lambda}\rangle + \epsilon|JM-\bar{\Lambda}\rangle], \quad (2)$$

where $\bar{\Lambda} = |\Lambda|$ and $\epsilon = \pm 1$. The parity of a state is given by its eigenvalue under the parity (space-fixed inversion) operator \hat{i} and thus we have

$$\hat{i}|JM\epsilon\rangle = \epsilon(-1)^J|JM\epsilon\rangle. \quad (3)$$

Thus within each Λ doublet of a given J , one level has even parity and the other has odd parity. ϵ is known as the parity index. Using current spectroscopic conventions, the $\epsilon = +1$ levels are designated as f and the $\epsilon = -1$ levels as e .¹² A recent study by Alexander and Dagdigan¹³ has clarified the physical nature of the electronic charge distributions in Λ -doublet functions and the e Λ -doublet level may be identified as that in which the electronic function is symmetric with respect to the plane of rotation whereas the f Λ -doublet level has an electronic function which is antisymmetric with respect to this plane.

The ground state in each of the molecules considered in this work is $^1\Sigma^+$ and hence each has even electronic parity. The parity of each ground state rotational level is given by $(-1)^J$. The electric dipole selection rules indicate that in a single photon process the following rules apply:

$$|+\rangle \leftrightarrow |-\rangle, |+\rangle \leftrightarrow ||+\rangle, |-\rangle \leftrightarrow ||-\rangle,$$

where the $|+\rangle, |-\rangle$ designations apply to overall parity (rotational \times electronic). Since there is necessarily a change in rotational parity on P or R excitation, one of these transitions will populate the e Λ -doublet component of the $^1\Pi$ excited state whereas a Q excitation will populate the f Λ -doublet component.

2. The propensity rules

The curious dynamical behavior of excited Π states has been the focus of much attention both theoretical and experimental. The topic is well described in the original literature and will not be discussed in detail here. The experimental results, which were obtained on a number of alkali diatomics,^{14–16} may be summarized quite succinctly. Alkali diatomics were prepared in single rotational levels of varying J values (e or f components) using discrete lines of an ion laser. Rotational energy transfer, due to collisions with a variety of rare gas and other nonreactive partners, was then studied using the intensities of spectrally resolved lines in the emission spectrum as a measure of the rate of transfer into the new quantum levels. Two distinct types of processes could be identified. These were: (i) rotationally inelastic collisions which preserved the initial Λ -doublet surface formed upon excitation, i.e., $\Delta J = \pm 2n$ for a homonuclear diatomic (leading to P and R doublet emission if the excitation was via P or R); (ii) rotationally inelastic transfer which changed the initial Λ -doublet quantum number, i.e., $\Delta J = \pm n$ where n is an odd integer for a homonuclear diatomic leading to Q emission following P or R excitation. The former are referred to as Λ -doublet surface preserving collisions and the latter as Λ -doublet surface crossing collisions. The first type of process was found to be quite normal in that upward and downward inelastic transitions ($\Delta J = \pm 2n$) were found to obey microreversibility, i.e.,

$$k_{J \rightarrow J'} = \frac{(2J' + 1)}{(2J + 1)} \frac{e_{J'}}{e_J} k_{J' \rightarrow J}, \quad (4)$$

where e_J is the kinetic energy of the diatomic molecule in rotational state J . Thus for high J and small ΔJ , only a very small difference between upward and downward transitions is predicted and observed¹⁷ for $\Delta J = 2$ transitions. The second type of process, the surface crossing collisions however, showed abnormal behavior in that upward and downward transition rates were in general, quite markedly different. The $\Delta J = \pm 1$ asymmetry was most pronounced and the ratio of rates $\Delta J_{+1}/\Delta J_{-1}$ was found to vary from 0.5 to 3.0, the actual value depending on the nature of the collision partner and on the initial rotational quantum number. Both e and f Λ -doublet components were affected, the rate ratio being approximately reversed by changing from e to f or vice versa.¹⁴ The effect was observable in heteronuclear diatomics also¹⁶ despite the increase in the number of channels open for rotational transfer consequent upon the reduced symmetry.

There have been numerous attempts to account for the results outlined above theoretically,^{15,18–22} the most recent being that by Lebed, Nikitin, and Umanskii²² but despite this degree of theoretical effort there does not appear to be a simple physical model which will account for the unusual behavior in terms of useful molecular parameters. This is particularly frustrating since on this occasion a simple laboratory frame experiment is yielding direct information on dynamical events in the molecule frame. The theoretical descriptions do not have relevance to the work described herein with the exception that a persistent feature is the so-called symmetric top model²² which has some features in common

with the mechanisms which we propose to account for the experimental observations made in this work.

3. The experimental results

The studies on the $\pm \Delta J$ propensities described above^{14–16} were mostly carried out in cells at fixed, and rather low (i.e., below 5 mbar), foreign gas pressures. We have carried out similar studies but over a much wider range of pressures and, in addition, have measured the polarizations of each resolved line following excitation with circularly polarized light. This work has been done with two alkali diatomics namely Na_2 and NaK using a variety of collision partners. In addition, a limited study of the heteronuclear NaLi was made. This work was carried out using stainless steel cells of heat-pipe design (though care was taken to ensure that they were not working in heat-pipe mode) and consequently, high pressures of foreign gas could be introduced into the cell. Most unexpected behavior was observed with certain foreign gases, which we now describe, and again it will be seen that it is the sensitive $\Delta J = \pm 1$ propensities which give clue to the presence of an unusual interaction.

Two types of unusual behavior were observed experimentally. The first and most striking observation concerned the rates of $\Delta J = \pm 1$ transfer, i.e., the relative intensities of the Q_{+1} and Q_{-1} peaks following P or R excitation. The second concerns the polarization ratio of the “parent” or resonance lines, which is found to increase at high pressures. At present we have no satisfactory explanation for this latter observation but it provides a useful indicator of unusual dynamical behavior since it occurs at approximately the same pressure as the other unexpected observation namely the change in the $\Delta J = \pm 1$ propensities.

An indication of unusual behavior is seen in the spectra shown in Fig. 1 which displays the dispersed emission spectra from $\text{Na}_2(A^1\Pi_u^+)$ in the presence of xenon gas following

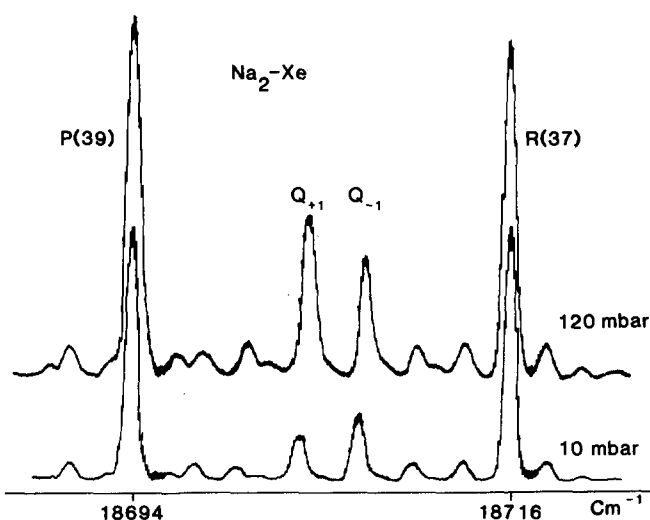


FIG. 1. Part of the rotationally resolved emission spectrum from $\text{Na}_2(A^1\Pi_u^+)$ following excitation into $J' = 38 v' = 9$. Excitation is via an R_1 transition using the line of an Ar^+ laser. Results are shown at two pressures of Xe gas, 10 mbar (lower curve) and 120 mbar (upper curve) and the change in relative intensities of the Q_{+1} and Q_{-1} lines can be seen clearly. Cell temperature 370 °C.

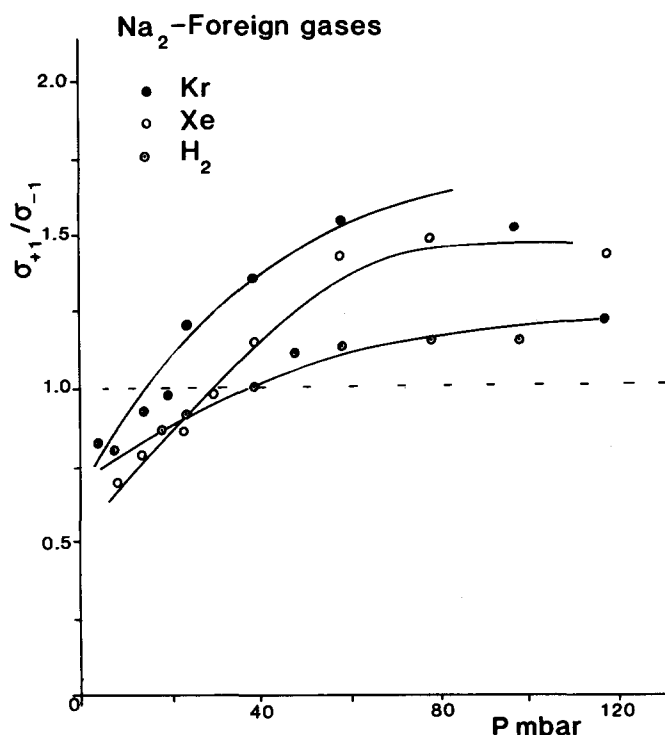


FIG. 2. Plot of the ratio of cross sections for $\Delta J = +1$ and $\Delta J = -1$ for $\text{Na}_2(A_1\Pi_u^+ J' = 38 v' = 9)$ vs foreign gas pressure for the three active gases Kr, Xe, and H_2 . Cell temperature 370 °C.

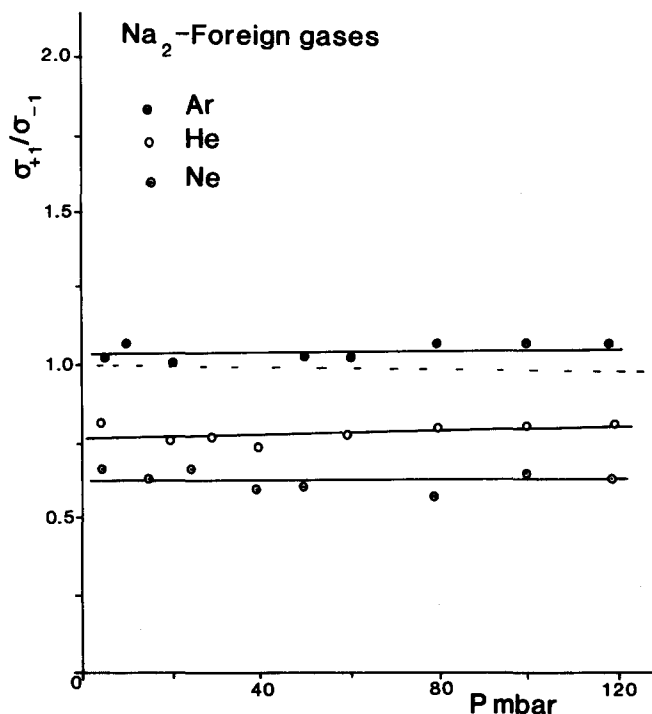


FIG. 3. Plot of the ratio of cross sections $\Delta J = +1/\Delta J = -1$ for Na_2 vs pressure of foreign gas for the three inactive gases Ar, He, and Ne. Cell temperature 370 °C.

excitation of the diatomic into the $J' = 38, v' = 9$ level. The excitation is via an $R \uparrow$ transition and thus the $e A$ -doublet level is populated and the Q_{+1} and Q_{-1} transitions represent the results of surface-crossing processes. Two sets of spectra are shown, the upper being intensity and polarization at relatively low xenon pressure (10 mbar) while the lower displays the resulting spectra in the high pressure regime, namely 120 mbar of xenon. The variation in the $\Delta J = \pm 1$ rates, i.e., the change in intensities of the Q_{+1} and Q_{-1} peaks can be seen very clearly. At high pressure, the magnitude of Q_{+1} has grown until it now exceeds Q_{-1} , which was the dominant channel at low pressure. A more quantitative representation of the pressure and foreign gas dependence of the $\Delta J = \pm 1$ propensities is shown in Figs. 2 and 3 in which Na_2 is again excited to $J' = 38, v' = 9$ of $B^1\Pi_u$. The ratio of the relative transfer rates for the two channels, k_{+1}/k_{-1} , is plotted as a function of foreign gas pressure to a total cell pressure of 120 mbar for six gases. Of these six gases, three, xenon, krypton, and hydrogen, are "active" in the sense that the ratio k_{+1}/k_{-1} changes with pressure while the remainder, He, Ar, and Ne are inactive, i.e., the relative rates into $+1$ and -1 channels are unchanged by pressure and the $+/-$ propensity is the same at all pressures observed. Similar results were obtained with NaK as the alkali diatomic excited to $J' = 102, v' = 10$ of $D^1\Pi$ though in this case the active collision partners were found to be Kr, Ar, and Xe while He, Ne, N_2 , CO_2 , and H_2 were inactive.

We should emphasize here that a study of the behavior of the separate channels indicates that the process is almost entirely one of *rotational excitation*. The increase of k_{+1}/k_{-1} is due to an increase in k_{+1} . The rate of transfer into

$\Delta J = -1$ is not greatly changed. More precisely one should say in the latter case for example, that the increase in the rate of transfer into the $\Delta J = -1$ level is matched by an approximately equal increase in the rate of transfer out of this level. Thus the overall result of the interaction with active gases is an increase in the rate of rotational excitation from the parent level with consequent A -doublet surface crossing.

These were bulk gas phase experiments using ion laser lines and thus the opportunities for variation of experimental parameters was limited. One possible variable of relevance is the kinetic energy of the species in the cell which is controlled by the cell temperature. It was possible to vary the cell temperature by around 100 °C and to still obtain results over a reasonable range of pressures. The result of this is shown in Fig. 4 where the trend is quite clear. Here $\text{Na}_2(J' = 38)$ is interacting with xenon and it is evident that the anomalous behavior sets in at much lower pressures when the temperature is lowered by 100 °C, indeed $k_{+1} > k_{-1}$ down to the lowest measureable foreign gas pressure at a cell temperature of 320 °C. The effect therefore is very temperature sensitive and increases as the kinetic energy of interacting species *decreases*. There is a similar trend in the NaK results but here the temperature range was much more limited because of the difficulty of observing NaK spectra over more than a very narrow temperature region.

The other variable, which is available through choice of exciting line is initial rotational state. Bergmann and Demtröder¹⁴ demonstrated that numerous rotational levels are accessible using different lines of the argon ion laser and thus a range of J' states is available. Several of these lines excite Q transitions while others excite P or R and thus it is possible to study the dynamical behavior of both e and $f A$ -doublet com-

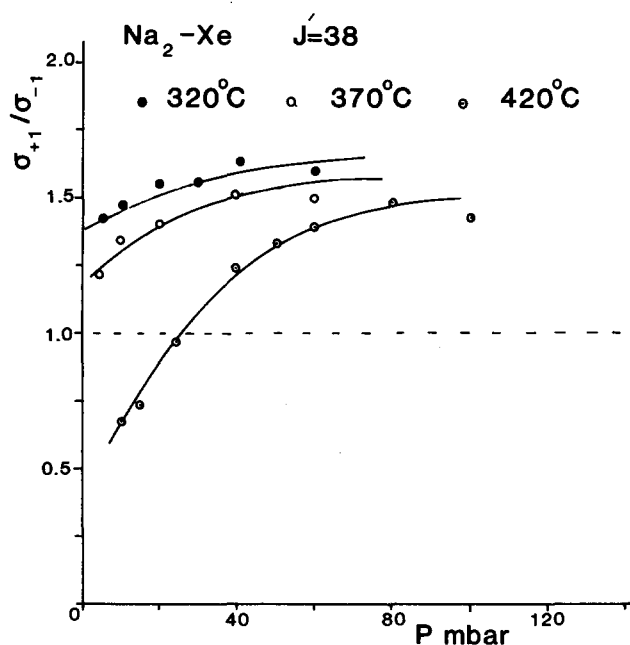


FIG. 4. Variation of cross-section ratio σ_{+1}/σ_{-1} in Na_2 as a function of xenon pressure for three different cell temperatures.

ponents as a function of pressure. We have found in Na_2 that there is no change in the k_{+1}/k_{-1} ratio as a function of pressure with any gas when the upper state is prepared by Q excitation. In other words, the unusual behavior with active gases is confined to the $e\Lambda$ -doublet surface only. The f level shows no such effect. This fact of course is immensely informative on the nature of the transient species which is formed.

Given the above restrictions, four different rotational transitions in Na_2 could be excited by P or R excitation and a small portion of these results is shown in Fig. 5 for Na_2 with Kr. It is seen that for this colliding partner the effect becomes more marked as the rotational quantum number decreases. This is not invariably the case and a more complex dependence was observed. This is summarized in Table I for the case of Na_2 and NaK. We have found that a useful indicator of the observed effect of rotational excitation as pressure increases is given by the adiabaticity parameter or the "reduced duration"²³ of the collision which is taken as the number of radians of rotation of the diatomic during the collision, i.e.,

$$\tau_J = \omega_J \times \tau_d, \quad (5)$$

where ω_J is the angular velocity of the diatomic and τ_d is the collision duration given by

$$\tau_d = l_c/v, \quad (6)$$

where v is the mean relative velocity of the colliding species and l_c is the interaction length over which the collision takes place. In this l_c was approximated by hard sphere radii. The angular velocity ω_J is defined by

$$\omega_J = \frac{2B_{ex}}{\hbar}(J + 1/2), \quad (7)$$

where B_{ex} is the rotational constant for the excited state of the diatomic.

The reduced duration is a function of diatomic rota-

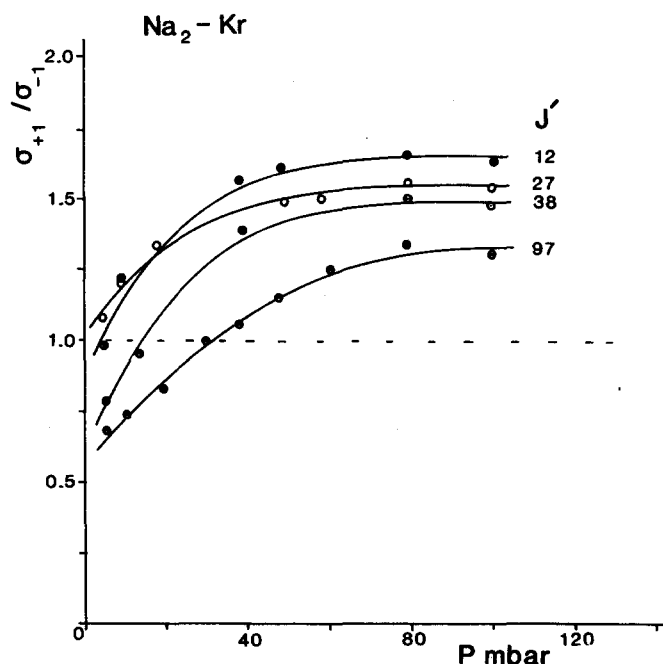


FIG. 5. Variation of σ_{+1}/σ_{-1} in Na_2 with Kr pressure for four different rotational states J' . These four levels are all accessed by P or R excitation and hence $e\Lambda$ -doublet levels are populated.

tional quantum number, cell temperature, and mass of collision partner. In Table I we list calculated reduced durations for the gases used in this study for the rotational levels of Na_2 and NaK which we have examined. The entries underlined represent that collision partner and rotational state for which the change in k_{+1}/k_{-1} was observed. An unmarked entry indicates that the state and gas were studied but no effect was observed. The remaining bracketed entries represent gases and rotational states as yet unstudied. The results of Table I suggest the following rough correlation that for the rotational excitation $\Delta J = +1$ effect to be observed one or both of the following conditions should be fulfilled. The collision should be "adiabatic," i.e., $\tau_J > 1$ and the collision partner must have a potential minimum with the excited

TABLE I. Table of values of reduced duration τ_J , (Ref. 23) for Na_2 and NaK in various J levels and with a number of foreign gases. Reduced duration is a measure of the "suddenness" of the encounter and a τ value greater than unity indicates an adiabatic interaction. The underlined entries are those diatomics, rotational levels, and collision partners which show the unusual dynamics. The other entries represent cases where the effect is not observed and the bracketed values indicate examples as yet unstudied.

Gas	$\text{Na}_2(370^\circ\text{C})$				$\text{NaK}(340^\circ\text{C})$	
	$\tau_{J=12}$	$\tau_{J=27}$	$\tau_{J=38}$	$\tau_{J=97}$	$\tau_{J=23}$	$\tau_{J=102}$
H_2	(0.08)	(0.18)	<u>0.25</u>	(0.63)	0.11	0.46
He	(0.11)	(0.23)	0.33	(0.83)	0.14	0.60
D_2	(0.11)	(0.25)	0.35	(0.88)	(0.15)	(0.52)
Ne	(0.21)	(0.47)	0.66	(1.66)	0.30	1.2
N_2	(0.28)	(0.62)	0.87	(2.22)	0.40	1.7
Ar	(0.28)	(0.62)	0.87	(2.20)	0.40	1.7
Kr	<u>0.34</u>	<u>0.75</u>	<u>1.05</u>	<u>2.67</u>	0.50	<u>2.1</u>
Xe	<u>0.39</u>	<u>0.85</u>	<u>1.19</u>	<u>3.01</u>	0.56	<u>2.4</u>

alkali which is deep compared to the mean thermal energy within the cell.

The final experimental indicator of unusual dynamical behavior comes from the polarization of the resonance line. As mentioned earlier, the excitation process in our experiment involves the use of circularly polarized light and in this process, a known but unsymmetrical distribution of M states is created in the upper level. Using the tensor density matrix formalism which we have described in a number of recent papers,^{9,24-27} when P or R transitions are excited with circularly polarized light, the upper level is highly oriented, the tensor density matrix elements ${}^J\rho_0^0$ and ${}^J\rho_0^1$ having nonzero values. The behavior of the resonance line circular polarization ratios (C) as a function of pressure has been thoroughly studied by us in the cases of I_2 ²⁴ and Li_2 ²⁵ and invariably it is found that the value of C diminishes very slowly as pressure is increased. In the case of the active gases in this work it was observed that after an initial slow fall in C with pressure, the circular polarization ratio began to rise as pressure continued to increase. This bizarre behavior was not observed with the inactive gases and was observed both in Na_2 and in NaK . Figure 6 illustrates this phenomenon for the $J = 38$ level of Na_2 in collision with Xe gas. As yet we have no explanation

for this behavior though it is evident that it is connected with the other odd observations since it occurs with the same active gases and at approximately the same pressures. It is possible that specific M states are active in the rotational excitation process that leads to an increase in the intensity of the Q_{+1} line but at present we have no experimental evidence for this. The Q lines are known to have inherently low circular polarization ratios²⁶ although their linear polarization values can be quite large. We have shown recently²⁷ that it is possible to measure linear and circular polarization ratios using the same (180°) experimental configuration. It would be valuable to study the transfer of population, orientation, and alignment in this way and we hope to report such a study in the near future. It should then be possible to follow the fate of each state multipole throughout the normal and the unusual energy transfer processes of these Π states. For the present we offer no explanation for the polarization results but simply take them as a further manifestation of a change in the dynamical behavior of the collision system.

In summary therefore the experimental results are as follows:

- (i) The rotational excitation $\Delta J = +1$ and Λ -doublet surface crossing rate increases more than does $\Delta J = -1$ when the pressure of certain collision partners increases.
- (ii) The excitation rate increase occurs only with the e Λ -doublet component of the excited Π state.
- (iii a) In order for the effect to be observed the collision should be in the adiabatic regime, i.e., $\tau_J > 1$, and/or
- (iii b) there should be a potential minimum of depth greater than or comparable to the mean thermal energy within the cell.
- (iv) The effect is increased when the kinetic energy of the colliding species is decreased.
- (v) The effect is accompanied by an increase in the polarization ratio of the parent line.

What kind of phenomenon can be invoked to account for these observations? All that changes throughout each experiment is the foreign gas pressure, i.e., the mean free path decreases and the number of collisions suffered by the excited species increases. Observations (iii) and (iv) above provide the main clues and these strongly suggest that a long-lived complex or orbiting resonance is involved. The arguments for this are as follows. The observation of anomalous dynamical behavior depends strongly on collision partner. Two factors can be identified: mass, which affects the reduced duration and intermolecular potential. The effect is strongly enhanced when the potential well is deep compared to the thermal energy and when the interaction is sufficiently slow for the atom to become trapped within this well. Thus reducing cell temperature, and hence mean kinetic energy, increases k_{+1}/k_{-1} dramatically, affecting particularly the pressure at which the effect becomes observable. Similar behavior is seen in the variation with rotational state. In general adiabatic interactions lead to the observed rotational excitation. Observation (ii) indicates strongly that a specific atom-alkali diatomic relative geometry favors formation of the long-lived complex.

Thus the postulated long-lived complex can account for

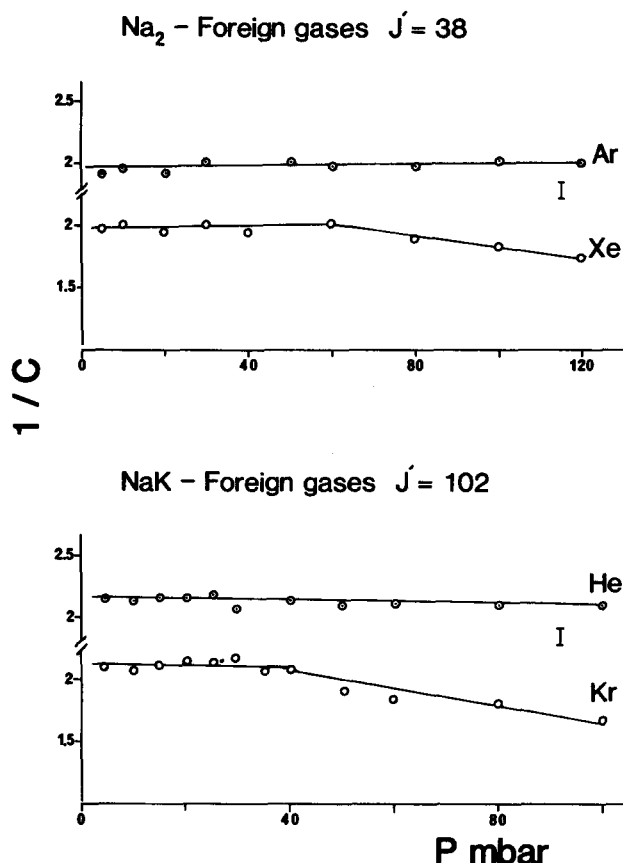


FIG. 6. Variation of circular polarization ratio of resonance lines of Na_2 and NaK with pressure. Results are shown for both active gases and inactive gases. The polarization ratio is plotted in the form $1/C$ vs pressure since through this plot the cross section for reorientation may be obtained, (Ref. 9). The unusual behavior referred to in the text is very clear in this plot as a downturn or negative reorientation cross section. As can be seen from the data, which are representative of numerous other such plots, the downturn is observed with NaK -Kr and Na_2 -Xe but not with the lighter rare gases.

the apparent increased rate of formation as cell temperature is lowered and the dependence of the k_{+1}/k_{-1} ratio on both collision partner and rotational level. The shape of the k_{+1}/k_{-1} vs pressure curve provides more difficulty partly because of the unknown time scale of the complex formation and decay. The scale of elapsed time that is known and which provides a reference timebase is the radiative lifetime. For alkali diatomics in excited Π states, the radiative lifetimes are typically of the order of 10^{-8} s. During this period, the long-lived complex will be formed and may decay many times but we sample over this entire period.

It is straightforward to calculate the probability that multiple collisions will take place during the lifetime of the excited state though the characteristic exponential decay of electronically excited species must be considered. For Na_2^*-Xe collisions at 40 mbar pressure of Xe, the probability of a second collision during the excited lifetime is approximately 15% of the probability of a first encounter.²⁸ At 60 mbar pressure the possibility of a third collision is finite and has risen to some 3% that of a single collision. The relevance of these calculations depends upon the lifetime of the complex species and this is quite unknown. Although experimental results are available^{1,4} on van der Waals molecules, they are of limited value here because they refer invariably to molecules in very low vibrational and rotational levels. A similar comment applies to theoretical estimates⁵ though we note the close-coupling calculation by Hutson, Ashton, and LeRoy⁵ on H_2-Ar predicts vibrational predissociation lifetimes of $> 20 \mu\text{s}$. Calculations by Hutson, Ashton, and Child predict rotational predissociation times of $\text{HCl}-\text{Ar}$ to be much faster but find that this rate decreases rapidly with increasing rotational quantum number.

The molecules considered here differ from those studied in supersonic expansions in that the diatomics are vibrationally and rotationally very hot. The effect of this on complex lifetime is unknown. If the complex can reasonably be considered as having a lifetime of the order of nanoseconds then the shape of the k_{+1}/k_{-1} vs pressure curve could be explained in terms of a complex formed initially by the capture in an orbiting resonance on collision, stabilized by an energy-removing second collision but then ultimately dissociating and/or undergoing destruction at higher pressures by further collisions. This however remains speculative. Clearly there will be an anticipated increase in complex formation as number density of active rare gas species increases and this may be solely responsible for the sharp initial rise of k_{+1}/k_{-1} vs pressure. At high pressures it is apparent that an equilibrium is reached between the rate of formation and the rate of destruction. More experimental data is needed before the shape of the pressure dependence curve may be fully explained.

Two further observations remain unexplained and these concern the quantum-selective aspects of the process, namely the fact that only the $e\ A$ -doublet appears capable of forming the long lived complex and also the curious selectivity in the rotational excitation which accompanies the process. These appear to involve more the geometry of the long lived species and the manner in which it may dissociate and we discuss these aspects in the following section.

B. Structure and rotationally selective dissociation of the long-lived complex

1. Structure of complex

First we consider if the Na_2X species is formed from ground state molecules, as in the case of I_2 -rare gas complexes,^{1,2} which are then excited and eventually dissociate, or alternatively if, as we assumed in the previous section, the complex is formed from excited alkali diatomics during the lifetime of the excited electronic state. The available evidence appears to favor the latter mechanism mainly on the grounds of depth of potential well. In NaAr for example D_e for $^2\Sigma$ is 40.4 cm^{-1} while that for $^2\Pi_{1/2}$ is 568.2 and $^2\Pi_{3/2}$ is 558.6 cm^{-1} . These are experimental measurements. Other values of potential minima are available from calculations by Baylis²⁹ which agree well with experiment where available for comparison. It is clear from these calculations that potential minima of the order of the cell mean thermal energy are available in excited Na atom-rare gas interactions. If we assume that the diatomic excited to the $^1\Pi_u$ state behaves like an excited 2P state alkali atom bonded to one in a 2S state, the alkali atom-rare gas potentials will give a reasonable estimate of the alkali molecule-rare gas minima. Thus we feel confident that the long-lived complex is formed from excited state alkali molecules.

The NaAr experiments and the calculations of Baylis also demonstrate that the $^2\Pi$ excited state is much more stable than the $^2\Sigma$ excited state and hence we can assume that it is the Π -symmetry overlap of the rare gas orbitals with the excited Na_2 orbital that gives rise to complex formation. Since we know that it is the $e\ A$ -doublet function only which exhibits complex formation and since we know that the $e\ A$ -doublet component is that which is symmetric to reflection in the plane of rotation of the molecule,¹³ we are now in a position to devise a plausible structure for the long-lived complex. This is shown in Fig. 7 for the case of an Na_2 -rare gas complex. The similarity between this proposed structure and the T-shaped van der Waals I_2-He molecule described by Levy¹ is clearly apparent. Here the donor-acceptor type of interaction suggested as a possible model for bonding in some van der Waals species³⁰ is also in evidence. In the case of the heteronuclear alkali diatomics the excitation will generally be localized much more on one of the alkali atoms and thus a more L-shaped complex with the rare gas would result.

As discussed earlier the lifetime of the transient species is not known nor is it easy to estimate. The excited lifetimes

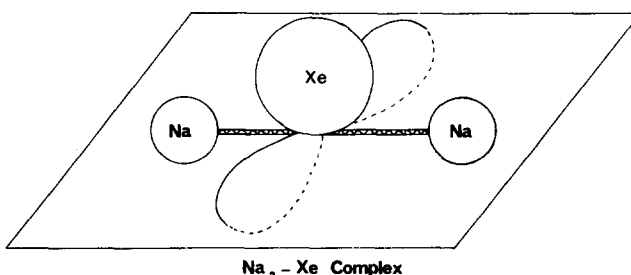


FIG. 7. Proposed structure of the long-lived complex formed between xenon and the $e\ A$ -doublet component of the $^1\Pi$ excited state of Na_2 .

of $^1\Pi_u$ electronic states in alkali diatomics are generally in the range of 10–20 ns and this gives an upper limit. In order to explain the characteristic rotational excitation observed in the experiments we assume the formation of a complex whose lifetime is at least long enough for a number of (low frequency) vibrations of the triatomic species. This does not seem physically unreasonable. If the complex has time to execute a number of vibrations then it is possible to regard decomposition of the triatomic molecule as a vibrational or a rotational predissociation and to consider in what way this process may lead to rotational excitation and surface crossing.

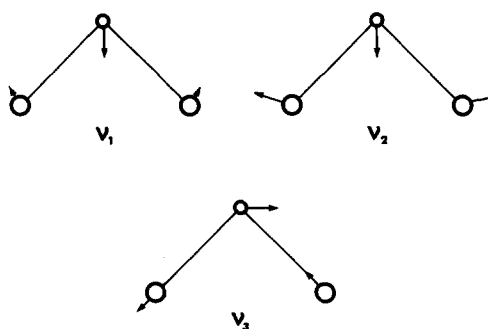
A very approximate estimate of the lifetime of the collision complex may be obtained from a simple RRK calculation of the unimolecular decay rate of the triatomic collision complex species. This is at best semiquantitative but is useful in giving some indication of approximate lifetimes. We use the expression³¹

$$\tau \approx 10^{-13} \left(\frac{E - \epsilon^+}{E} \right)^{1-s}, \quad (8)$$

where E is the total energy of the complex, ϵ^+ is the well depth and s is the number of vibrational modes of the complex. The model is not truly appropriate for such a simple system but some interesting results emerge particularly when comparison is made with the time taken for a full rotation of the diatomic molecule. For example, experimental work with NaK was limited to two rotational levels, $J' = 23$ and $J' = 102$ of $^1\Pi$ and, as described earlier, observation of changes in dynamical behavior with pressure are limited to $J' = 102$. Rotational periods for these two levels are calculated to be 1.21×10^{-12} s for $J' = 23$ and 2.73×10^{-13} s for $J' = 102$. The calculated RRK lifetimes vary with collision partner and are 1.19×10^{-13} , 1.07×10^{-13} , 4.49×10^{-13} , 9.54×10^{-13} , and 2.65×10^{-12} s for NaK with He, Ne, Ar, Kr, and Xe, respectively. It is striking that only in the cases of Ar, Kr, and Xe are the calculated unimolecular decay rates such that the complex is predicted to have a lifetime which is longer than a rotation period. This applies only to the $J' = 102$ level of the two examined and it is with just these gases that the long lived complex is observed. Similar results are obtained with Na₂ and rare gas collision partners. We should perhaps not deduce too much from these necessarily crude calculations but the results do suggest that the lifetime of the complex is at least as long as a rotation period. Thus there is time during the existence of the complex for it to execute a number of vibrations in each mode.

2. Rotationally selective predissociation of complex

Upon formation of the long lived complex by capture within the potential well of a rare gas atom, the translational degrees of freedom of the atom are converted into internal modes of the new triatomic. It is straightforward to show that one of these new internal modes will be a rotation while the others will be vibrations. A triatomic of the structure shown in Fig. 7 has C_{2v} symmetry (it will be lower in the case of the heteronuclear diatomics but we begin by considering the case of Na₂). The problem now becomes similar to the predissociation of the I₂–He complex considered by Levy



Vibrational modes of Cl₂O

FIG. 8. Normal vibrational modes of a triatomic species belonging to the symmetry group C_{2v} such as Cl₂O (taken from Herzberg).

and co-workers¹ except that in our case the diatomic is initially in a high rovibronic level and the end result is a rotational excitation rather than the vibrational deactivation which characterizes the I₂–He decomposition. It may not be strictly correct to ascribe to this complex, normal mode behavior with symmetry designations of the C_{2v} group and a picture in which stretch and bend modes do not mix. However, this is a convenient starting point and has the advantage that we may compare the apparent dissociative mode with that which appears to prevail in I₂–He.

When the complex is formed, two new vibrational modes are introduced and the other degree of translational freedom which is lost on complex formation goes into rotation about the new y axis. The symmetry species of these two vibrational modes are A_1 and B_2 , the latter representing the antisymmetric stretch mode, a kind of hindered rotation. The new rotational motion has B_1 symmetry. The three vibrational modes are shown in Fig. 8 taken from drawings by Herzberg³² of normal modes in the molecule Cl₂O. Clearly, the two A_1 modes ν_1 and ν_2 cannot lead to rotational excitation. These represent extensions and contractions of the weak bond (and of the chemical bond) and despite being the apparent candidates for breaking the transitory bond, do not appear to be active in this instance. The B_2 mode (ν_3), however, consists of a rotary motion about the x axis and dissociation in this mode could lead to changes in the rotational energy of the diatomic “fragment.” In the case of the long lived alkali diatomic–rare gas complex, this must represent the main dissociation mechanism.

The antisymmetric stretch dissociation proposed above cannot be the only process involved however and some other, almost simultaneous, motion must contribute. This follows from the fact that none of the vibrational modes ν_1 – ν_3 of the C_{2v} molecule can give rise to A -doublet surface crossing, a distinctive feature of the experimental evidence we have presented for the existence of a long lived complex. In order to induce surface crossing a rotatory motion about the y axis is needed, i.e., an out-of-plane bend of the rare gas atom relative to the alkali diatomic. Such a motion would have B_1 symmetry in the C_{2v} point group and the evidence points to the new rotational mode created when the complex is formed. Thus the separate normal mode picture cannot be sustained in this instance since simultaneous rotational exci-

tation and Λ -doublet surface crossing is observed and the dissociative mechanism giving rise to the excited products must be some complex mixture of the new antisymmetric stretch and the new γ axis rotation. This mixing of modes may of course come about through the complex having lower symmetry than C_{2v} . Clearly the heteronuclear diatomics cannot have C_{2v} symmetry and indeed the complex is likely to be L -shaped in this case rather than T -shaped since the excitation will be located on one or other of the alkali atoms. It may however be that the antisymmetric stretch and the rotational mode have roughly similar frequencies and the motions become extensively mixed through Coriolis interactions. It is difficult to estimate possible vibrational frequencies for this complex. In Cl_2O and F_2O , ν_3 has the highest frequency of the three modes but there are too many unknown factors to use this as a reliable criterion concerning the long lived diatomic-rare gas species involved here.

The new rotational motion of the diatomic which results from this proposed dissociative mechanism is about a different axis to the original molecular rotational motion and involves a reorientation of the rotational angular momentum vector. This may be related to the unexplained polarization changes which were mentioned above and are evident in Fig. 6. This also would suggest that the plateau in the k_{+1}/k_{-1} vs pressure curve has significance in connection with the complex dissociation since it occurs at approximately the same pressure as the upturn in the polarization ratio.

In the heteronuclear diatomics NaK ($J' = 102$) and NaLi ($J' = 30$) we have observed a small but distinct increase in the $\Delta J = 0$ surface crossing transition at high pressures and this process may result from dissociation via a rotational mode, presumably that introduced when the translational energy of the atom is converted to internal rotational energy.

IV. CONCLUSIONS

A number of unusual experimental phenomena have been observed in alkali diatomic-foreign gas interactions as the pressure of foreign gas is increased. The main observation is a change in the rate of $\Delta J = \pm 1$ rotational transfer such that rotational excitation becomes dominant. This occurs only with certain gases and for diatomics in certain rotational states. Analysis shows that these are the gases for which the potential minimum is greater than the mean thermal energy of molecules within the cell and that the rotational states are those for which the collisional interaction is in the adiabatic regime. The rotational excitation always involves Λ -doublet surface crossing and occurs only when the e Λ -doublet component is initially populated. The effect is strongly enhanced by reduction in cell temperatures. An unexplained reduction in parent line polarization appears to accompany complex formation.

We have proposed that an orbiting resonance or long-lived complex is the cause of this behavior. Its suggested structure is shown in Fig. 7. We suggest that dissociation of the long-lived species is mode selective and this results in rotational excitation upon dissociation.

It is striking that this observation of an orbiting resonance has been made in the bulk gas phase albeit with quan-

tum-selected molecular species. The observation has been made through the existence of the Λ -doublet components which are characteristic of an electronic Π state, particularly through the very sensitive Λ -doublet surface crossing transitions. It is probably the case however that the phenomenon is not unique to Π states and was observed in this instance because of the deep potential minima existing for some of the collision partners used in this study with the Π state of the alkali diatomics. It is likely that the effect will also be observable in Σ states particularly at low temperatures provided the criteria mentioned above are met. This latter statement remains to be tested however.

One consequence of the known Π state electronic distributions is that we can move rapidly from a laboratory-fixed observation to a molecular frame interpretation and we have used this to propose a structure for the long-lived species and a mechanism for rotational excitation in its predissociation. We hope that further experiments will test these proposals and that more rigorous theoretical models will be presented to explain the observations we describe.

One cannot help but speculate that orbiting resonances of this type must have a very profound effect on the dynamics of gas phase species in bulk media. Resonance phenomena have been known from theory for a number of years but little experimental evidence has been forthcoming. The rotational state selectivity we have observed is most unexpected and the consequences for bulk gas phase behavior particularly at low temperatures are quite far reaching.

The orbiting resonance process described herein leads to the preferential population of the upper Λ -doublet component of a rotational level of the Π electronic state, in a manner which may be M selective.

There are possible astrophysical consequences of the observations we report here, and the activity of H_2 in this regard and also the increase in efficiency of the process as temperature is lowered are significant. We discuss the relevance of these observations to OH maser action in a forthcoming article.³³

ACKNOWLEDGMENTS

We thank the Science and Engineering Research Council for support of this project and the Government of Iraq for research studentships to FJMA and MSM. We also thank Dr. S. Bosanac, Dr. A. J. Stace, and Dr. B. J. Whitaker for valuable discussions on the results presented here and Professor M. H. Alexander for a preprint of Ref. 13.

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