Direct observation of the picosecond dynamics of I\textsubscript{2}-Ar fragmentation

J. J. Breen, a) D. M. Willberg, M. Gutmann, b) and A. H. Zewail
Arthur Amos Noyes Laboratory of Chemical Physics, c) California Institute of Technology, Pasadena, California 91125

(Received 27 August 1990; accepted 3 October 1990)

The fragmentation of van der Waals (vdW) complexes offers an opportunity for studying the half-collision dynamics in well-defined systems. In previous work from this laboratory, we have studied, in real time, the dynamics of the “half” and the “full” collision, but we had no results on the diatom–rare gas small vdW complexes. Iodine with rare gases I\textsubscript{2}-M (M = He, Ne, and Ar) are of particular interest for a number of reasons.

First, the I\textsubscript{2}-M vibrational dynamics are rather simple; an iodine stretch, and two van der Waals’ stretch and bend modes. Second, from the pioneering work on the spectroscopy, there is a wealth of data that provide the vibrational structure, geometry, and the photochemistry of these systems. Third, the I\textsubscript{2} real-time dynamics on the fs-ps time scale have already been reported. Finally, unlike the case of large molecules, theory is quite advanced for these smaller systems, and there is hope for a detailed understanding of IVR and vibrational predissociation. Real-time studies of large vdW complexes have been reported for isoquinoline, tetrazine (in S\textsubscript{1} and S\textsubscript{0}), phenol, cresol, perylene, stilbene, aniline, and (NO\textsubscript{2})\textsubscript{2} (in S\textsubscript{0}), and only recently have results become available for the family of halogens. With nanosecond lasers, the lifetime of ICI-Ne in its A state was measured to be 3±2 ns for ν’ = 14 by the Lester group. As discussed below, other methods, such as linewidth measurements, have been used to deduce vibrational predissociation lifetimes.

In this communication, we report direct picosecond measurements of the state-to-state rates obtained from real-time observation of fragment I\textsuperscript{+} molecules in the reaction

\[
\begin{array}{ccc}
\text{I} & \overset{\text{Ar}}{\longrightarrow} & \text{I}^* \rightarrow \text{I}^* + \text{Ar} \\
\hline
\text{I} & \text{*} & k (v' = n; v' = n - 3) \\
\text{Ar} & \text{*} & \text{I} \\
\end{array}
\]

On the picosecond time scale, we observe the exponential buildup of nascent I\textsuperscript{+} population, and the experiments show a slow “inverse” dependence on v’, i.e., a slight decrease in the rate with increased v’. The results give the homogeneous width of the initial state, and establish the time scale for the dynamics in the channels, I\textsuperscript{+} + Ar (vibrational predissociation, k\textsubscript{v}) and I + I + Ar (electronic predissociation, k\textsubscript{e}). The rise times measured in our experiments correspond to τ = (k\textsubscript{v} + k\textsubscript{e})\textsuperscript{-1}, and for the above reaction, n = 21 and 18 in the B state of I\textsubscript{2} (or I\textsubscript{2}-Ar). The binding energy of I\textsubscript{2}-Ar is known to be between 220 to 226 cm\textsuperscript{-1}; at the vibrational levels that we access in this experiment, this requires the redistribution of at least three quanta of energy from the iodine to the van der Waals bond in order to induce dissociation. (The geometry is not known from our experiments, but we draw it to be nonlinear, as suggested by previous work.)

The experiments required a special care, because of inherent difficulties in preparing “clean” complexes (usually much weaker than the parent species) with no background and at the same time detecting them with high enough sensitivity for state-to-state measurements on the picosecond time scale. The pump–probe scheme applied in these molecular beam experiments is similar to that used in earlier developments. The temporal resolution is limited only by the pulse widths of the lasers. We used the first pump pulse to excite the complex to a given vibrational state (v’\textsubscript{1}). The delayed probe pulse was used to excite the nascent I\textsuperscript{+} fragment from a given vibrational state (v’\textsubscript{2}) to a low-vibrational state in the known higher energy ion-pair state (see Fig. 1). The transients, which give k (v’; v’\textsubscript{f}), are recorded by monitoring the UV emission from the ion-pair state, while varying the temporal delay between pump and probe laser pulses in a Michelson interferometer arrangement before the molecular beam apparatus.

The assignment of the states involved was checked in a
FIG. 1. Schematic of the fragmentation channels and energetics of the I₂-Ar system. (Left) shown are the two fragmentation channels I₂-Ar → I₂ + Ar and I₂-Ar → 2I + Ar, and the scheme of the experiments. The pump wavelength was 5555.5 Å for v' = 21 and 5642.5 Å for v' = 18 experiments. The probe wavelength was 3416.0 Å and 3370.5 Å, respectively. (Right) shown are the different vibrational levels of the relevant I₂-Ar states, together with the constant energy exit channels for nascent I₂ (indicated by a horizontal arrow). The dissociation energies are D(X) = (234.2 ± 240.1) cm⁻¹ [Ref. 15(b)] and D(B) = (220 ± 226.3) cm⁻¹ [Ref. 15(b)]. The total energy in the B state is E. Hence, E + E₂ gives the energy deposited in I₂-Ar. There is ≈ 51 cm⁻¹ of energy available for recoil when, v' = 21 is excited, i.e., E - D(B).

A least squares fit of the transient gives the rise time of nascent I₂ to be 77±8 ps. Therefore, the k(v' = 21; v'' = 18) is (77)⁻¹ ps⁻¹. We repeated these experiments, but at different energy spanning the v' = 18, and we found k(v' = 18; v'' = 15) to be (70)⁻¹ ps⁻¹ (the actual rise is 70±11 ps).

Two questions are of interest here: (i) how do these measurements, when translated to the homogeneous broadening, compare with spectroscopic data, and (ii) what is involved in the dynamics to give these rates and their v' dependence? For I₂-Ar, our measurement of 77 ps translates to a width of 0.07 cm⁻¹. The 77 ps time constant is consistent with the lower limit estimate of 30 ps for I₂-Ar, v' = 15, obtained from linewidth measurements. This lifetime estimate from the linewidth, as discussed in J. Chem. Phys., Vol. 93, No. 12, 15 December 1990.
FIG. 2. Picosecond state-to-state rates of the I₂-Ar system. Shown are the transients obtained using the pump-probe scheme described in the text. The results are given for the \( v'=21/v_f=18 \) experiments; top is the bare iodine transient for calibration \( (B, v_f=18) \), middle is the \( \text{I}_2-\text{Ar}-\text{I}_2+\text{Ar} \) transient, bottom is the visible cross correlation. The dashed lines show fits to an exponential rise function. For bare iodine, these fit yield, as expected, a very fast rise, determined by the laser pulse widths. The dip on the \( \text{I}_2 \) transient is the result of rotational coherence, and will be discussed in detail in Ref. 13.

Ref. 15(a), is only valid if the observed linewidth is free of rotational congestion (in contrast, in \( \text{I}_2-\text{He} \), the rotational levels were resolved\(^{(19)} \)). As known in the literature for vdW systems,\(^{(20)} \) only when the spectral width is homogeneously broadened\(^{(21)} \) can one deduce the lifetime. Comparison with time-resolved data is then possible. Reference 20 gives a good account of the work in this area of linewidth measurements.

Theoretically, the dynamics of predissociation of \( \text{I}_2-M \) has been addressed by the groups of Jortner,\(^{(22)} \) Beswick,\(^{(22)} \) Ewing,\(^{(23)} \) Rice,\(^{(24)} \) and others. Basically, the following simplified picture can address the physics of the problem. The system may be divided into the I-I stretch, which is an “intramolecular” mode, and the vdW mode(s) which are “intermolecular.” The predissociation is the result of the coupling between the intramolecular and intermolecular modes, coupled to the translation continuum. Energy gap law,\(^{(22)}(b) \) momentum gap law,\(^{(23)} \) Rice, Ramsberger, Kassel, and Marcus (RRKM),\(^{(25)} \) and alternative RRKM\(^{(24)} \) descriptions have been derived to express the rates of predissociation and product state distributions in vdW complexes. Recent full 3-D quantum calculations\(^{(26)} \) have provided a more rigorous treatment of the close coupling problem and there is now hope for quantitative comparisons with experiments.

The \( \text{I}_2-\text{Ar} \) system has two channels for fragmentation, the vibrational and electronic predissociations. Measurements\(^{(15)(a)} \) of the fluorescence intensity of \( \text{I}_2 \) produced after the vdW complex is excited, as a function of increasing vibrational excitation, showed strong oscillations that were not found for other \( \text{I}_2-M (M=\text{He}, \text{Ne}) \) systems. Quantitative absorption spectra\(^{(27)} \) (intracavity) have also shown these oscillations. The oscillations were attributed to variations in the electronic predissociation rates resulting from the crossing of the \( B \) state with the repulsive \( \Pi \) state(s).

Since we know the state-to-state rates, we can now relate them to the product state distributions. By a simple kinetic treatment,\(^{(7)} \) we find that the ratio of the vibrational predissociation rate constant \( k_v \) \( (v_f'=21,v_f'=18) \) to \( k_s \) \( (v_f'=18; v_f'=15) \) is about 2.9. Accordingly, \( k_s \) is increasing with higher \( v' \), while the electronic predissociation rate constant is increasing with lower \( v' \). The latter may explain why \( \text{I}_2-\text{Ar} \) complexes have not been seen at lower \( v' \)'s, and is consistent with the quantum yield results of Atkinson.\(^{(27)} \)

The system, of course, is a quantum mechanical one and the justification for applying simple kinetics is not at all obvious. However, the presence of the dissociation continuum makes the coherence decay very fast, and the use of kinetics more plausible. This inference will be tested in further experiments. The kinetic scheme considers the two channels, shown in Fig. 1 \( (k_v \) and \( k_s) \).

The fluorescence of either the complex \( \text{I}_2-\text{Ar} \) (rate \( k_f \)) or \( \text{I}_2 \) (rate \( k_f' \)) occurs on a much longer time scale (i.e., \( k_v \) \( \gg k_s \) \( k_f' \)), but was also considered as part of our scheme. The time dependence of nascent \( \text{I}_2 \) can be expressed as follows:

\[ \text{J. Chem. Phys., Vol. 93, No. 12, 15 December 1990} \]
formalism. To relate to the time-integrated fluorescence measurements, we now consider the ratio of the fluorescence from \( I^{2-} \) produced from predissociating \( I^{2-}-Ar \), to that of bare \( I^{2-} \). The fluorescence arises mainly from the \((\nu' - 3)\) channel, as shown in Ref. 2. We, therefore, obtain the following expression for the ratio, as measured by Levy and co-workers:

\[
F(\nu') = \frac{C_k}{k_0 + k_e} = Ck_e \tau, \tag{2}
\]

where \( \nu' \) is the vibrational level originally excited in the complex (I\(_2\)-stretch) and \( C \) is a parameter that depends on the relative concentrations and Franck-Condon factors involved. If the presence of the Ar atom does not alter the Franck-Condon factors (I\(_2\)-stretch vibration), as was also assumed in Ref. 15(a) and confirmed in Ref. 27, we obtain:

\[
\frac{F(\nu' = 21)}{F(\nu' = 18)} = \frac{k_e(\nu' = 21, \nu_f = 18)}{k_e(\nu' = 18, \nu_f = 15)} \frac{\tau(\nu' = 21, \nu_f = 18)}{\tau(\nu' = 18, \nu_f = 15)}. \tag{3}
\]

The values of the \( F \)'s are reported in Ref. 15(a), and from our \( \tau \) values the ratio of the \( k_e's \) can now be determined. The important point to note here is that the time-resolved data give the total (\( k_0 + k_e \)) quantity, and with product-state distribution data, a ratio of \( k_e's \) can be deduced.

The values of \( k_e \) we derive are consistent with theory in that they show an increase with \( \nu' \), and in fact they scale directly, and with product-state distribution data, a ratio of \( k_e's \) can be deduced.

The magnitudes of \( k_e's \), however, deserve some comment. The theoretically calculated rate constants depend crucially on the parameters chosen for the vdW potential \( I^2/Ar \), usually assumed to be a Morse-type potential. For the complex in a linear geometry, Beswick and Jortner\(^{2(b)} \) predict a lifetime of about 25 ps for \( \nu' = 20 \) in its \( B \)-state, using a dissociation energy \( D = 200 \text{ cm}^{-1} \) and an inverse length parameter \( \alpha_{ArI} = 1.25 \text{ Å}^{-1} \). Distorted wave\(^{2(b)} \) and numerical calculations in the close coupling formalism\(^{2(b)} \) yield comparable results. However, changing \( \alpha \) to 2.02 Å\(^{-1} \) gave \( \tau < 10 \text{ ps} \) for \( \nu' = 2 \), which is far too small; for \( \nu' = 21, \tau \) is expected to be lower than 10 ps by orders of magnitude. The noncollinear calculations for \( I^2-\text{Ar} \) are not known, but it has been shown\(^{2(b)} \) that for \( I^2-\text{He} \), \( k_e \) becomes about an order of magnitude smaller for noncollinear calculations when compared with the collinear ones. Transferring this idea to the \( I^2-\text{Ar} \) case yields \( \tau \approx 250 \text{ ps} \) \((\nu' = 20, \alpha_{ArI} = 1.25 \text{ Å}^{-1}) \) and \( \tau < 100 \text{ ps} \) \((\nu' = 2, \alpha_{ArI} = 2.02 \text{ Å}^{-1}) \), a change in the right direction, but far from bridging the gap with experiments on \( \nu' = 21 \) or 18. This, of course, is a simplistic view, and more accurate calculations, with the correct geometry, are needed.

With the same parameters as in Ref. 22(c), Gray and Rice\(^{24} \) reported Fermi golden rule (FGR), classical dynamics (CD), and alternative RRKM (ARRKM) calculations for a collinear \( I^2-\text{Ar} \). For \( \nu' = 2 \), they have shown \( \tau \approx 6 \text{ ps} \) (CD), \( \tau \approx 8 \text{ ps} \) (FGR), \( \tau \approx 4.5 \text{ ps} \) (ARRKM). These numbers are very consistent, but far too small, as \( k_e \) grows nonlinearly with \( \nu' \). Gray and Rice showed the dependence of \( k_e \) on the potential of the vdW mode in their CD calculations. However, this dependence can help the discrepancy by only an order of magnitude. It appears, therefore, that the potential parameters need to be changed for closing this gap between theory and experiments, and 3-D calculations should be consistent with this change. The dependence on \( \nu' \) is less of a problem.

The effects of anharmonicity of the intramolecular bond vibration on the behavior of \( k_e \) vs \( \nu' \) was investigated theoretically, and a superlinear dependence was found.\(^{22(b),22(e)} \) In Table I of Ref. 22(e), data for \( k_e's \) (collinear geometry) are given. From the data, a ratio \( k_e(\nu' = 20)/k_e(\nu' = 15) = 5.6 \) can be obtained. Assuming a \( \nu' \) dependence of \( k_e \) on \( \nu' \) within this region \((20^\circ/15^\circ = 5.6) \), yields \( k_e(\nu' = 21)/k_e(\nu' = 18) = 2.5\) which is not too far away from our finding of 2.9 (vide supra).\(^{28} \) Further experiments are in progress to quantify this \( \nu' \) dependence.

In these prototype vdW systems, there is now a wealth of experimental and theoretical work to be pursued. We plan to monitor the atomic iodine to address the electronic predissociation problem. We also plan to extend the measurements to other energy ranges of \( I^2-\text{Ar} \) and to larger complexes to reach the \( I^2-\text{M} \) limit for comparison with \( I^2 \) in Ar\(^{29} \) and recent \( I^2-\text{CO}_2 \) cluster experiments.\(^{30} \)

Note added in proof: After the submission of this communication, we have made several new observations for the \( I^2-\text{Ar}_2 \) and \( I^2-\text{Ne} \) systems. The rise time of nascent \( I^2 \) in the \( I^2-\text{Ar}_2 \) is faster than that in the corresponding \( I^2-\text{Ar} \) system, consistent with increased electronic predissociation. For the \( I^2-\text{Ne} \), the vibrational predissociation and its \( \nu' \) dependence is directly measured. These experiments will be reported in a forthcoming publication.

This work was supported by the National Science Foundation.

---

1 For a recent review, see L. Khundkar and A. H. Zewail, Annu. Rev. Phys. Chem. 41, 15 (1990), and references therein.


17 The rise of nascent $J^+$ was assumed to be exponential, and the zero of time was taken from the best fit. In future work, we will determine the $t = 0$ point to insure that there is no time lag.
18 For the 21/18 experiments, both the $v = 0$, and the $v = 3$ vibrational levels of the $f$-ion-pair electronic state were probed. The measured rise time of the nascent $J^+$ for both probe wavelengths were the same within experimental error.
28 In Ref. 4, Beswick and Jortner quoted a private communication with D. H. Levy, stating that the vibrational predissociation rate, $k_v$, shows a dependence which is approximately proportional to $v$. This would yield a ratio of $k_v(v'=21)/k_v(v'=18) = 2.2$, which is also in fair agreement with our finding.