Complex Resonances in the Predissociation of Cs_2

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We present detailed quantum mechanical analysis of the complex resonances observed in molecular predissociation. The complex features in the photodissociation spectrum of Cs_2 are reproduced well by the close-coupling calculation including three channels. A very narrow resonance with a linewidth of $\sim 2\times10^{-7}$ cm^{-1} is predicted. It is shown that q reversal can occur in predissociation with only two channels involved.

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When a particle collides with another that has internal structure, temporary quasistationary states can be created. These short-lived intermediaries are called resonances, which contain detailed information on the connecting paths between the initial and final states. When the outcome of the collision process involves either breaking or formation of chemical bonds, this quasistationary state is often called a "transition state" or "transition-region species." In the study of molecular reaction dynamics, the resonance can be a very sensitive probe of the reactive scattering processes. The resonance observed in the predissociation of diatomic molecules is the simplest example of such transition-region species. While there are close similarities between the diatomic predissociation and the atomic autoionization, the presence of nuclear degrees of freedom in molecules makes the dynamics of predissociation more complicated than that of autoionization.

Fano showed that when a single discrete state is coupled to a single continuum, the absorption line shapes can be described by a simple formula, known as Beutler-Fano profile [1]. In real atoms or molecules, however, multiple autoionization or predissociation pathways are often available. The constructive or destructive interferences between these ionization or dissociation pathways result in more complex resonance structures, which is called a "complex resonance," or "overlapping resonance" [2]. Although several examples are found in autoionization [3], such complex resonance has not been seen in predissociation. Very recently, we have observed the complex resonance in the predissociation of Cs_2 [4]. This Letter presents the first detailed quantum mechanical analysis of the complex resonances occurring through multiple predissociation pathways.

Among alkali dimers, Cs_2 shows the most complex absorption bands due to very compact potential energy curves and large spin-orbit couplings. They are, therefore, suitable to study the predissociation occurring through multichannel interactions. We have designed a new high temperature pulsed beam machine and successfully prepared a very cold molecular beam of Cs_2 [5,6], in which all the vibrational hot bands are practically eliminated and the rotational temperature is reduced to about 1 K. The dramatic cooling in a pulsed molecular beam turns out to be very important in the study of resonance in molecules, since comparison of the observed photodissociation spectrum with theory becomes much simpler with only a limited number of partial waves contributing to the total cross section.

Figure 1(a) shows an experimental photofragment yield (PFY) spectrum of Cs_2, in which the Cs $(6\,^2P_{3/2})$ atoms resulting from the photodissociation of Cs_2 are selectively monitored by single photon ionization. This experimental PFY spectrum clearly shows asymmetric line profiles. The most striking feature in this PFY spectrum is a repeated gradual change of the line shapes in series B from red-shaded to blue-shaded, and then to

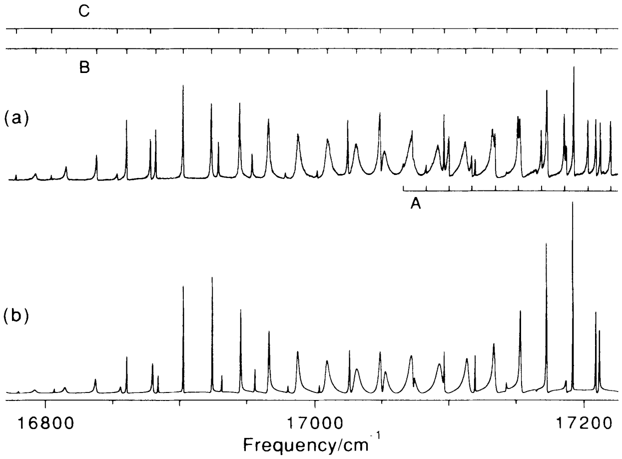

FIG. 1. (a) Experimental photofragment yield spectrum obtained by selectively monitoring the Cs $(6\,^2P_{3/2})$ fragment. The rotational temperature in the beam was about 1 K. (b) Calculated spectrum convoluted by laser linewidth and the rotational state distribution of the initial state assuming a rotational temperature of 1 K.

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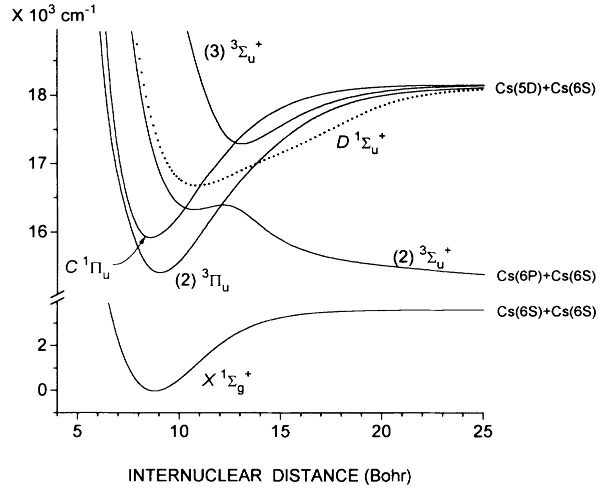

FIG. 2. Potential energy diagram of Cs_2, from the *ab initio* calculations of Spiess and Meyer (Ref. [8]).

red-shaded. Strong multichannel interference is seen for the resonance near 17050 cm^{-1}. The bands in the A series are due to the Cs^+ ions resulting from the fragmentation of the $Cs_2{}^+$ ions generated by two photon ionization, and correspond to the vibrational progression of the $D\ ^1\Sigma_u{}^+$-X transition.

Figure 1(b) presents the calculated photodissociation cross section, convoluted by assuming a Boltzmann distribution at $T_r = 1$ K and a Gaussian laser profile. We solved the close-coupled Schrödinger equation to obtain the predissociation cross section [7]. The line shapes and intensities of most of the resonances, including very weak ones, are very closely reproduced by the calculation. Figure 2 shows the potential energy curves of Cs_2 in the frequency range of interest, which are used in the calculations. The potential curves are from the *ab initio* calculations by Spiess and Meyer [8]. Some potential curves are modified slightly to give better agreement with the experimental spectrum [9]. The available spectroscopic data on these electronic states are fragmentary. Only the low vibrational levels of the $C\ ^1\Pi_u$ (up to $v' = 13$) [10] and $2\ ^3\Pi_u$ states (up to $v' = 6$) [6] were observed by the earlier experiments. The $\Omega = 0$ component of the $2\ ^3\Pi_u$ state is known to perturb the $D\ ^1\Sigma_u{}^+$ state at frequencies higher than 17500 cm^{-1} [11].

In the calculation of the dissociation cross section shown in Fig. 1(b), we included a single open channel, corresponding to the $2\ ^3\Sigma_u{}^+$ state, and two closed channels, corresponding to the $C\ ^1\Pi_u$ and $2\ ^3\Pi_u$ states. Among these three electronic states, only the $C\ ^1\Pi_u$ state has nonzero transition dipole moment with the ground state of $^1\Sigma_g{}^+$ symmetry. At the observed frequency range, only the $2\ ^3\Sigma_u{}^+$ state has a good Franck-Condon overlap with the ground state ($v'' = 0$). The resonances in Fig. 1 are then described as a result of interactions among a dark continuum, dark discrete states near the resonance, and remote bright discrete states.

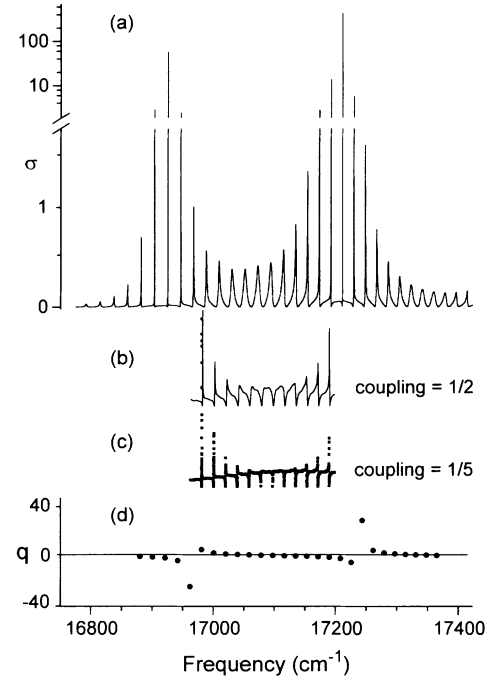

FIG. 3. (a) Calculated PFY spectrum with only 2 channels corresponding to the $2\ ^3\Sigma_u{}^+$ and $2\ ^3\Pi_u$ states included. Electronic transition moment is only given to the $2\ ^3\Sigma_u{}^+$-X transition. (b) Same as (a) with spin-orbit coupling reduced to 1/2 of the *ab initio* values used in (a). (c) Same as (a) with spin-orbit coupling reduced to 1/5 of the *ab initio* values. (d) q values calculated by Eq. (1).

The calculated dissociation cross section, before convolution, predicts many very narrow resonances, which become much wider after the convolution [Fig. 1(b)]. The resonance observed at 17002.03 cm^{-1} has a calculated linewidth of 2.5×10^{-7} cm^{-1}, with an intensity 5 orders of magnitude higher than those of typical broad resonances. The estimated predissociation lifetime is ~20 μsec. Compared with some broad resonances, this is more than 6 orders of magnitude enhancement of the predissociation lifetime. These very narrow resonances have been observed in atomic autoionizations [12], and are interpreted to occur when the coupling matrix element of the resonance to the open channel is accidentally canceled out due to interferences from multiple ionization pathways.

In Fig. 3(a), we present the result of two-channel close-coupling calculations, which include only the $2\ ^3\Sigma_u{}^+$ and $2\ ^3\Pi_u$ states. The potentials and magnitude of the coupling are the same as those used for the calculation in Fig. 1. Nonzero electronic transition moment is explicitly given to the $2\ ^3\Sigma_u{}^+$ state to represent the oscillator strength borrowed from the $C\ ^1\Pi_u$ state. This two-channel calculation reproduces the series B of the experimental PFY spectrum in Fig. 1(a) very well. While it is often suggested that asymmetric resonance profiles are observed when both of the continuum and discrete states have oscillator strengths, the calculated PFY spectra of Fig. 3 show that asymmetric line shapes can result from the interaction between the dark discrete state and bright continuum. This is because the discrete state is modified by an admixture of continuum, the contribution of which to the transition matrix element ($\langle \Psi_E | T | i \rangle$) interferes with that of the continuum [1].

The *ab initio* values of the spin-orbit coupling between the $2\,{}^3\Pi_u$ and $2^3\Sigma_u{}^+$ state is of the order of ~ 60 cm^{-1} [8]. When the resonance width, which is related to the magnitude of coupling, is comparable to the spacings between the adjacent resonances, the resulting line shapes can be strongly affected by the neighboring resonances through second order interactions [2]. In order to show how this overlapping affects the resonances, we present the dissociation cross sections calculated with the magnitude of the spin-orbit coupling between the $2\,{}^3\Sigma_u{}^+$ and $2\,{}^3\Pi_u$ states reduced to 1/2 and 1/5 of the *ab initio* values in Figs. 3(b) and 3(c), respectively. We obtained the line shape parameter q by fitting these spectra to the Beutler-Fano profile, and compared them with those directly calculated by the formula

$$q = \frac{\langle \varphi | T | i \rangle + P \int dE' \langle \varphi | H | \psi_{E'} \rangle \langle \psi_{E'} | T | i \rangle / (E - E')}{\pi \langle \varphi | H | \psi_E \rangle \langle \psi_E | T | i \rangle}, \qquad (1)$$

where $|\varphi\rangle$ represents the discrete state, $|\psi_{E'}\rangle$ is the continuum, $|i\rangle$ is the initial state, T is the transition operator, H is the interaction operator, and P denotes the principal part of the integral [1,13]. This formula applies when a single discrete state interacts with a continuum. $\langle \varphi | T | i \rangle$ is negligible in the present case, and thus set to vanish in the calculation. The q values calculated from Eq. (1) are plotted in Fig. 3(d). These q values agree well with those obtained by fitting the calculated cross section in Fig. 3(c), where the coupling is reduced to 1/5 of the *ab initio* values. The deviations between the fitted and calculated q values become larger as the coupling is increased. Apparently, the q values and line shapes of the observed resonances, as seen in Fig. 3(a), are considerably deviated from those of the isolated resonance case. For these overlapping resonances, the line shape needs to be described by a set of q values, each of which represents the contribution of the participating resonances [1]. Interestingly, many resonances in Fig. 3(a), particularly narrow ones, could still be very well described by the Beutler-Fano profile.

Figure 3(d) shows that the value of q, obtained by Eq. (1), changes gradually along the series of resonances, and the sign is reversed 3 times in the given frequency range. The q values obtained by fitting the line shapes in Fig. 3(a) show similar oscillations as in Fig. 3(d). Such change of the sign of q is called "q reversal." While the q reversal in autoionization is considered as the result of three-channel interactions [2,3], Fig. 3 shows that in predissociation the q reversal may occur with only 2 channels involved. This can be ascribed to the properties of the continuum. As shown in Eq. (1), the value of q depends on the coupling matrix element between the continuum and discrete state, $\langle \psi_E | H | \varphi \rangle$. In predissociations, if the potential curves cross at the outer limb, $\langle \psi_E | H | \varphi_v \rangle$ is expected to show oscillatory variations with change of v [14,15]. In contrast, $\langle \psi_E | H | \varphi_n \rangle$ in autoionization is proportional to $(n^*)^{-3/2}$ [15], showing a monotonous variation with n^*, the effective principal quantum number. Note that the resonance width, Γ, is proportional to the square of $\langle \psi_E | H | \varphi \rangle$.

In summary, we have shown that the complex resonance features in the predissociation of Cs_2 is well described by the interferences among three channels. A very narrow and intense resonance with a linewidth of $\sim 2 \times 10^{-7}$ cm^{-1} is predicted. It is shown that q reversal in predissociation can occur from the interaction of only two channels.

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