Multichannel quantum interference in the predissociation of Cs$_2$:
Observation of $q$-reversal in a complex resonance

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State selective photofragment yield spectrum is obtained in the 580 nm system of Cs$_2$ by monitoring Cs $(6^2P_{3/2})$. Strongly asymmetric line shapes are observed and interpreted as being due to resonances. We observed a gradual sign change of the Fano line shape parameter, which is called “$q$-reversal”, for the first time in predissociation. Some of other lines show complex line shapes that cannot be fitted by a usual Beutler–Fano profile. These complex line shapes may be attributed to the interfering resonances.

When two particles (either atoms or molecules) collide with each other, a quasibound state can be formed, which is generally known as a transition state or an activated complex among chemists. Alternatively, one can prepare the quasibound state in a well-defined manner by the absorption of photons, or by the electron-detachment of an anion, provided that the quasibound state has a good Franck–Condon overlap with the initial state. This quasibound state is called a “resonance” in a more general term, which occurs when discrete quantum states interact with continua. In solids, the continuum provided by the conduction band or phonons may cause resonances. In the study of molecular reaction dynamics, the resonance can be a very sensitive probe of the reactive scattering processes, providing spectroscopic information on the detailed process of chemical changes. In certain cases, selective control of the reaction pathway becomes possible through resonances.

In the simplest case of an isolated resonance, where a single discrete level (associated with a closed channel) interacts with a single continuum (an open channel), the absorption cross section can be described by a Beutler–Fano profile. This has the form

$$\sigma(\epsilon) = \sigma_0 \frac{(q+\epsilon)^2}{1+\epsilon^2},$$

where $\epsilon = (E - E_0) / (\Gamma / 2)$ is the reduced energy, $\Gamma$ is the width of the resonance, $\sigma_0$ corresponds to the dissociative continuum cross-section, and $q$ is the line shape parameter. When more channels are coupled together, or when the resonance is not isolated, the resonance structure becomes complicated and cannot be fitted to the above formula. This type of resonance is called as a “complex resonance” or “overlapping resonance”. Occasionally, one can observe interesting phenomena such as the $q$-reversal, in which a gradual sign change of $q$ occurs. In this Communication we report the first clear observation of this “complex” resonance and $q$-reversal in molecular photodissociation.

Alkali dimers provide a good system to study the collision dynamics of open shell atoms. They produce photodissociation fragments with nonzero angular momentum. Since the alkali dimers only possess two valence electrons, theoretical treatments of these systems are generally simpler than those for other diatomics. Collins et al. reported that Cs$_2$ photodissociates into excited Cs atoms in different internal states when illuminated by blue or orange light. Detailed spectroscopic studies of the photodissociation of Cs$_2$ have been hampered, however, by the complex absorption spectrum caused by hot bands. We have recently built a new high temperature pulsed nozzle, which is extremely effective in reducing the internal temperatures of the alkali dimers. Using this very cold beam, we investigated the predissociation of the 580 nm system of Cs$_2$, which has been extensively studied in recent years.

Details of the experimental setup will be given in a forthcoming paper. A very cold pulsed beam of Cs$_2$ is produced by expanding Cs vapor with Kr. The pulsed jet was collimated by a 1.2 mm diam skimmer 5 cm from the nozzle. An excimer laser pumped dye laser prepared Cs$_2$ in its excited state, which then predissociates into an excited and a ground state Cs atom. The excited Cs atoms thus produced were selectively ionized by a second dye laser, which was pumped by the same excimer laser. The Cs$^+$ ions were detected by a time-of-flight (TOF) mass spectrometer. The two laser beams were copropagating with a delay of about 5 ns. The wavelength of the photodissociating laser was calibrated by simultaneously obtaining an optogalvanic spectrum with a Ne cell. The bandwidths of the pump and probe lasers were about 0.2 cm$^{-1}$.

Figure 1 shows the photofragment yield (PFY) spectrum of Cs$_2$ monitored by Cs $(6^2P_{3/2})$. Cs$_2$ was expanded with 1 atm of Kr. The major species in the molecular beam were Cs$_2$, Cs, and Kr. The wavelength of the photodissociating laser was scanned, while the wavelength of the ionizing laser was fixed at 541 nm, which provided just enough energy to ionize Cs $(6^2P_{3/2})$. The photodissociating laser can produce neither Cs $(5^2D_{3/2})$ nor Cs $(5^2D_{5/2})$ in the scanned wavelength region, since its energy is lower than the thermodynamic thresholds for the production of these excited atoms. Three vibrational progressions were observed in this spectrum and are tagged as “A”, “B”, and “C” in the figure, respectively. The A progression corresponds to the $D^1Σ^+_u-X^1Σ^+_g$ transitions. The identities of the B and C progressions are not clear and they might correspond to new electronic states which were not observed previously. The rotational temperature of Cs$_2$ in the...
molecular beam is estimated to be $-0.5$ K by simulating the rotational contours with the known molecular parameters of the $D$ and $X$ states. No hot bands are observed in this spectrum, and the vibrational temperature is thus estimated to be lower than 5 K.

Figure 2 shows the PFY spectrum obtained at similar experimental conditions, except that the wavelength of the ionizing laser increased to 513 nm, at which Cs ($6^2P_{3/2}$) cannot be ionized. The $A$ progression is still observed, while the $B$ and $C$ progressions completely disappear. The Cs$^+$ signal which is observed in Fig. 2 seems to originate from the fragmentation of the Cs$_2^+$ ions that were generated by 1+1 resonance enhanced multiphoton ionization. When the ionizing laser was blocked, no Cs$^+$ signal was observed.

The broad lines of the $B$ progression show clearly asymmetric line shapes. The most striking aspect of Fig. 1 is the gradual change of the line shape from red-shifted to symmetric, to blue-shifted, and then to red-shifted again. The possibility that the asymmetric line shapes are due to rotational structures is excluded based on the following evidences. Firstly, the vibrational progression $B$ shows very regular vibrational spacings. Rotational bands for diatomic molecules are blue-shifted when the rotational constant of the excited state is larger than that of the ground state, i.e., $B' > B''$, and red-shifted when $B' < B''$. The rotational constant ($B'$), however, would not change so widely in a region where the potential energy curve is close to harmonic. Secondly, if the broadening is due to rotational structures, its shape will change when the rotational temperature of the Cs$_2$ in molecular beam is changed. When the rotational temperature is increased from 0.5 K to 5 K by decreasing the backing pressure, the band shape remained the same. Thirdly, Cs$_2^+$ signal was detected for narrow bands in progression $B$, but not for the broad bands, suggesting that the lifetimes of the broad bands are much shorter than the duration of the excitation laser pulse (a few nanosecond). Lastly, the band at 17 050 cm$^{-1}$ (indicated by an arrow) shows a large dip in the center, which cannot be explained by a rotational structure.

The most plausible explanation for these asymmetric line shapes is given by the resonances. Figure 3 shows fittings of the line shapes to a Beutler–Fano profile. The line shape parameter, $q$, is also listed along with the figures. The solid line is a simulated spectrum assuming a Beutler–Fano profile, which describes well the observed spectrum represented by the dots. In order to be more accurate, the effect of the distribution of the rotational levels in the initial state needs to be included in the simulation. When the width of the Beutler–Fano profile is large (greater than 1.5 cm$^{-1}$ as in the shown examples), however, the resulting absorption spectrum convoluted by the rotational structure shows practically the same shape as the unconvoluted single Beutler–Fano profile. This is due to the compact rotational structure caused by the ultralow rotational temperature of the Cs$_2$ (0.5 K). When the width of the profile ($\Gamma$) is smaller, the overlapped rotational transitions cause apparent broadening of the resonances.

The shading of the line shape depends on the sign of $q$. The value of $q$ is negative for red-shifted lines, and positive for blue-shifted lines. Clearly, $q$ changes sign twice in the spectrum shown in Fig. 1. Such a sign change of $q$ is called “$q$-reversal”. The $q$-reversal may occur in two ways; one by the gradual change of $q$ through a zero and the other through a pole of $q$ as a function of energy. While several examples of the $q$-reversal have been observed in autoionization spectra, this is the first observation of the $q$-reversal in predissociation. The $q$-reversals in the autoionization of the 3-channel system have been studied theoretically by using multichannel quantum-defect theory (MQDT). These studies show that the $q$-reversal in autoionization can occur when there is a third perturber or
an “interloper”. An important question is raised here as to what causes the \( q \)-reversal in molecular predissociation. In the autoionization case, the interloper is a lower level of a third Rydberg series, which is well separated from the adjacent levels of the same series, whereas in molecular predissociation the closed channels correspond to vibrational progressions, of which adjacent levels are rather closely spaced. There is a possibility that the continuum might be structured by itself and take the role of an interloper in predissociation.

Another interesting feature is seen in a line centered near 17 050 cm\(^{-1}\). This feature, because this is a very clear manifestation of the multichannel character in the resonances. It is quite a coincidence that a \( q \)-reversal occurs around here. Note that the \( B \) and \( C \) progressions fall on the same position near the location of another \( q \)-reversal (around 16 900 cm\(^{-1}\)). These observations may become the key to understand the whole problem.

The rich features observed in the complex resonances of \( \text{CS}_2 \) contain a wealth of dynamical information about the exact shapes of potential energy curves, curve crossings, and interchannel couplings, because the line shapes are the direct results of the quantum interference between coupled channels. They should provide a good touchstone for the theoretical studies of the resonances. More detailed analysis of these Fano profiles and the \( q \)-reversals observed in the 580 nm system of \( \text{CS}_2 \) will be given in a forthcoming paper.\(^{26}\)

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