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Double Resonance Spectroscopy and Molecular Dynamics

Cun-Hao Zhang and Guo-He Sha

During the past two decades, numerous laser spectroscopic techniques have been introduced that aim at unraveling the structure and dynamics of excited molecular species. The technique of optical-optical double resonance multiphoton ionization (OODR-MPI) has been one of the latecomers of the family. It is, nevertheless, also one of the most promising.

Even for simple molecules, electronic spectra tend to be so complex that it is difficult to properly assign the transitions, in spite of the fact that data may be taken at a resolution sufficient to see molecular rotations. Double resonance spectroscopy, developed by Field and co-workers (*1*), proves to be an incisive tool in this respect. Here, we are dealing with two consecutive resonance transitions involving three molecular energy levels, 1, 2, and 3. In general, double resonance experiments are performed as follows: First, a tunable laser is locked to the frequency of a known molecular transition 1 → 2. Thanks to the narrow linewidth of state-of-the-art tunable lasers, this can easily provide finer-than-rotational spectroscopic resolution. Scanning the wavelength of a second tunable laser then gives rise to a very simple, easy-to-interpret spectrum of 2 → 3, as a result of the restricted selection rules of 1 → 2 → 3. By tuning the first laser to successive rovibronic transitions of 1 → 2 and repeating the scanning of the second laser, one can accumulate systematic and unambiguous spectroscopic data of 2 → 3.

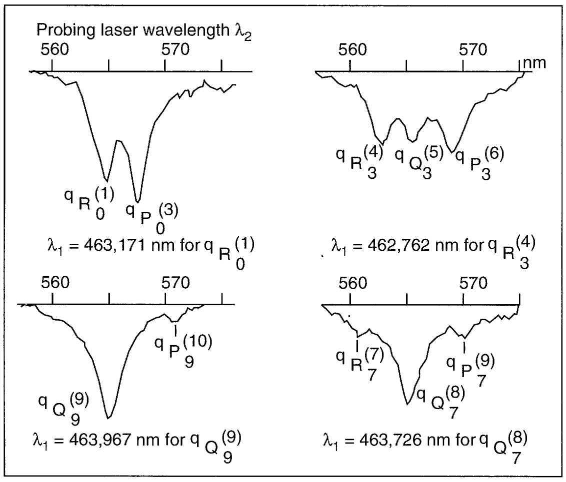

Fig. 1. Ion dip spectrum for NH$_3$ $\tilde{C}'\,^1A_1$ $v' = 1 \rightarrow {}^1A_2''$ $v_2'' = 1$ transitions obtained by locking the $\tilde{C}' \leftarrow \tilde{X}$ pump laser and scanning the probe laser (*4*).

Multiphoton excitation by tunable lasers in the optical region (*2*) allows access to high-lying electronic states of molecules, which would have required very expensive tunable vacuum ultraviolet light sources. Ionic detection competes favorably with photon counting; with a little care and a number of simple tricks, the former is capable of providing higher signal-to-noise ratios and higher sensitivity. These features combine to make OODR-MPI an extremely versatile spectroscopic technique, whose potential has not yet been fully exploited.

We have used a variant of OODR-MPI known as ion dip spectroscopy (IDS) to obtain rotational spectra of the very short-lived predissociating species NH$_3$ $\tilde{A}$ $^1A_2''$. Ito and co-workers have performed detailed studies on large molecules by IDS (*3*). Our present endeavor deals with a short-lived species with a lifetime of around 10^{-13} s (*4*). Each rotational line is broadened to several tens of wave numbers because of the short lifetime, and in conventional spectroscopy there is always complete overlap of the rotational lines with the adjacent ones to form a diffuse spectrum. With IDS, we first performed three-photon excitation to pump ground state NH$_3$ to the $\tilde{C}'$ state, and from there, another photon brought it to the ionization continuum. Then, with the first laser locked to a specific rovibronic transition $\tilde{C}'(v', J') \leftarrow \tilde{X}$, we scanned a second laser to bring about the stimulated emission $\tilde{A}(v, J) \xleftarrow{h\nu} \tilde{C}'(v', J')$. IDS is in essence an ionic detection version of stimulated emission pumping (SEP) first developed by Kinsey, Field, and their colleagues (*5*). Whenever the second laser hit such a transition, the $\tilde{C}'(v', J')$ species would have an additional depletion channel besides the usual one going to ionization, which caused a dip in the ion signal (Fig. 1).

Although IDS lines of iodine were obtained earlier (*6*), the lines in our spectra for NH$_3$ were much more pronounced, owing to the fact that the $\tilde{A}$ state predissociates fast enough to make the reverse process $\tilde{A} \rightarrow \tilde{C}'$ very unlikely. We worked out the selection rule that for each $\tilde{C}' \leftarrow \tilde{X}$ rovibronic transition, the follow-up $\tilde{A} \leftarrow \tilde{C}'$ transitions could be at most three, and these were readily assignable. It was also simple to determine the line center positions. Accordingly, a "composite" rotational spectrum could be constructed (Fig. 2), and the rotational constants B and C and the band origins could be obtained by least-square fits. Noting that for many molecules, the first excited electronic state is a short-lived predissociating state, our method should work for many of them, as long as their lifetimes are longer than a few tens of femtoseconds.

Once we found the vibrotational levels of the NH$_3$ $\tilde{A}$ state with IDS, we proceeded to explore the $\tilde{B}$ state by straight double resonance $\tilde{B} \leftarrow \tilde{A} \leftarrow \tilde{X}$ (*7*). Because $\tilde{B}$ is a degenerate electronic state, Jahn-Teller splitting can occur as a result of coupling between the electrons and nuclear vibrations. If the levels were purely vibrational, the symmetry should be E. Owing to the Jahn-Teller effect, however, each of these levels splits into E and A. Thanks to the OODR technique, we actually observed this splitting by distinguishing vertical bands of PQR structure, characteristic of E symmetry, from parallel bands of PR structure, characteristic of A symmetry. By these means, we successfully studied the Jahn-Teller effect rotationally, assigning each type of band

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and evaluating the vibronic coupling parameters (*7, 8*).

We went a step further with this method to study the Jahn-Teller–induced Fermi resonance (*8*). Previously, Fermi resonance was studied only in the ground electronic state and was allowed only between vibrational modes of the same symmetry. Now, because of Jahn-Teller splitting, new types of Fermi resonance become allowed between certain vibrational levels of the excited electronic state, $\tilde{B}$. This Jahn-Teller–induced Fermi resonance is termed nonadiabatic Fermi resonance and is in some cases governed by novel selection rules.

The technique of OODR-MPI as applied by us in dynamics studies is essentially a version of the widely used pump-and-probe technique but may also be grouped into the broad realm of double resonance. Collisional energy transfer processes have also been studied with this method in great detail. In a static sample cell, we vary the pressure of the sample gas as well as that of the collider, usually a rare gas, such that only single collision is experienced within the interval of the laser pulsewidth. First, a laser is locked to a specific quantum transition, $A(v, J) \leftarrow X$, usually of subrotational resolution. Then, as a second laser scans, the ion signal spectrum shows in addition to the parent lines a host of daughter lines as a result of collisional energy transfer. From the intensity ratio of daughter to parent lines, absolute energy transfer cross sections are computed. Furthermore, propensity rules can be inferred (*9*). With CO $A^1\Pi$ and $e^3\Sigma^-$ states as the model species, we have investigated several "subrotational" processes, such as rotational energy transfer (RET) with Λ doublet parity change or conservation (*10*), RET within a triplet (for example, F2 → F1, F2, or F3) (*11*), singlet-triplet intersystem crossing (*12*), rovibronic energy transfer between CO A and CO X (*13*), and collisional angular momentum reorientation of CO $A^1\Pi$ by He (*14*).

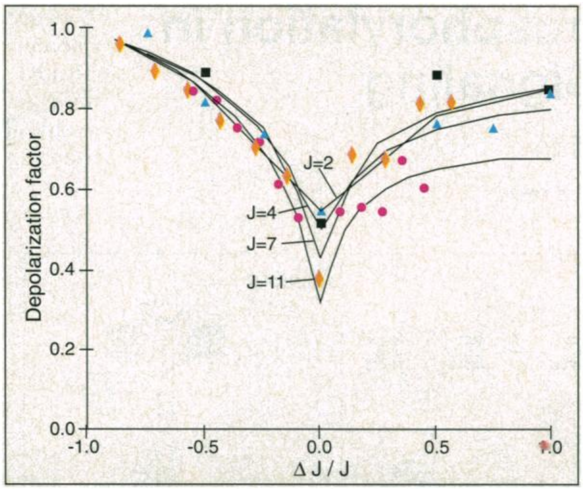

Fig. 3. The curves show the calculated depolarization factor *D* of CO (A)-He collisions derived with use of equation 16 of (*14*) for different initial *J* levels at temperature *T* = 253 K. Experimental data points: (■), *J* = 2; (▲), *J* = 4; (◆), *J* = 7; and (●), *J* = 11. We have found that the best fit between the experimental data and calculated curves is obtained when the impact parameter *b* = 2.9 Å. The corresponding collision cross section πb^2 = 26.4 Å^2, which is close to the total CO ($A^1\Pi$, v = 3) + He collisional rotational energy transfer cross section (28 Å^2) (*14*).

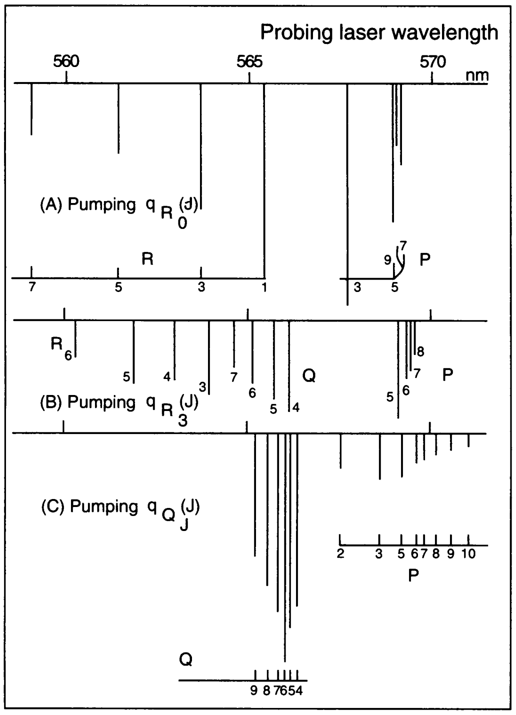

Fig. 2. "Composite" spectrum of NH_3 $\tilde{C}'\,{}^1A_1$ $v_2' = 1 \rightarrow {}^1A_2''$ $v_2' = 1$ transitions. The bars give position and relative intensity of the individual lines (*4*).

The latter type of experiment could be a precursor to the study of steric effect in chemical reactions, a subject of much recent interest, as shown in the excellent reviews by Zare and his coworkers (*15*) and Bernstein *et al.* (*16*). First, we create a highly oriented array of CO (A, v, J, M) species, where the population distribution of the quantum numbers M (where $M = -J, -J + 1, \ldots, J - 1, J$) is an indication of the anisotropy of the array, by two-photon pumping of ground-state CO with either a left-handed or right-handed circularly polarized laser. On the basis of the theory advanced by Bray and Hochstrasser (*17*), we are able to probe the orientation distribution of parent (J, M) and daughter (J', M') levels by measuring the corresponding intensity ratios (S_P/S_R) of the respective P and R branch lines. We define a normalized depolarization ratio D, which is related to (S_P/S_R) of both the parent and daughter lines and is averaged over right- and left-handed circular polarizations. If the orientation is completely conserved through the collision, we have $D = 0$. Conversely, if the collision causes complete randomization of the orientation, then $D = 1$. So we measure $(S_P/S_R)_{\sigma+}$ and $(S_P/S_R)_{\sigma-}$ for transitions of different J and ΔJ, and from this we calculate D and find a strong monotonic dependence of D on $|\Delta J|/J$. Because in a classical picture $|\Delta J|/J$ is a measure of the relative change in the vectorial angular momentum, it is indeed conceivable that D should be strongly related to $|\Delta J|/J$. More quantitative treatment based on the quantum scattering theory developed by Alexander and Davis (*18*), which is further simplified by an exponential energy-gap term to represent the dynamic effects, is found to fit nicely into the D versus $|\Delta J|/J$ experimental plot (Fig. 3).

In conclusion, OODR-MPI spectra have opened several ways to understand various spectroscopic features of the excited electronic state for a few molecules. There should be enormous opportunity for OODR-MPI in exploiting the spectroscopy and dynamics of other molecular species, and there is no reason why it is not going to find wider application in the next decade.

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