

Hydrogenic Rydberg States of Molecular van der Waals Complexes: Resolved Rydberg Spectroscopy of DABCO-N₂

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The complementary threshold ionization techniques of MATI and ZEKE spectroscopy have been used to reveal well-resolved, long-lived ($>10 \mu\text{s}$) hydrogenic Rydberg series ($50 \leq n \leq 98$) in a van der Waals complex formed between a polyatomic molecule and a diatomic molecule for the first time. The series are observed within 50 cm^{-1} of the adiabatic ionization threshold as well as two core-excited thresholds corresponding to excitation of up to two quanta in the van der Waals vibrational mode.

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Rydberg electrons can provide a sensitive probe of the electronic structure of an atomic or molecular core. Short range intracore interactions are best sampled by core penetrating Rydberg states ($\ell \leq 3$) but it has been argued that core nonpenetrating Rydberg states ($\ell > 3$), which by definition only sample long-range multipole moments and polarizabilities, provide a particularly clear view of the electronic structure of the core [1]. Rydberg-Rydberg transitions in high- ℓ states have been studied directly in a number of atoms [2–4] as well as in molecular hydrogen [5,6] but, in general, high- ℓ molecular Rydberg states are often extremely difficult to access directly [1]. However, a contrasting perspective can be obtained from a study of very high- n core nonpenetrating Rydberg states which become increasingly *less* able to distinguish the structural characteristics of a molecular core from that of a hydrogenic atomic core with increasing n . Such states can be accessed indirectly, close to the ionization threshold via a mechanism involving electric field induced ℓ and m_ℓ mixing in core penetrating optically bright states [7]. Observation of perturbations to such molecular nonpenetrating Rydberg states might then be viewed as a test of their sensitivity to the structure and electronic characteristics of the molecular core.

The energy of a polyelectronic atomic Rydberg state is given to a good approximation by the Rydberg formula

$$E_n = -\frac{R}{(n - \delta)^2},$$

where R is the reduced mass adjusted Rydberg constant, n is the principal quantum number, and δ is the quantum defect. For molecular Rydberg states the same formula can be applied for sufficiently high values of n . In either case, quantum defects obtained from fits of experimental term values to the Rydberg formula provide an indication of the value of the orbital angular momentum quantum number, ℓ , appropriate to a particular Rydberg series. The closer to zero the larger the value of ℓ and the greater the resemblance to the one-electron atomic model in

which the electron moves in a Coulombic potential of a point charge.

Atomic Rydberg series progressions have long since been used as a means to measure ionization energies of polyelectronic atoms. More recently the development of new threshold ionization techniques such as ZEKE (zero electron kinetic energy) [8] and MATI (mass analyzed threshold ionization) [9,10] spectroscopy has led to the observation of similar high- n Rydberg series in small molecular systems [1,11–13]. However, somewhat unexpectedly, finely resolved very high- n Rydberg structure has also been observed in a small number of larger polyatomic molecules [14–16], demonstrating that from the perspective of a nonpenetrating high- n electron, the structure of the molecular core recedes to resemble an atomic point charge. This premise has very recently been extended by Neusser and co-workers in their resolved Rydberg spectra of the benzene- X ($X = \text{Ne}, \text{Ar}, \text{Kr}$) van der Waals complexes [17,18]. They demonstrated that molecular complexes whose center of mass deviates markedly from the center of charge can also show a well-resolved Rydberg structure with apparently little evidence of perturbation to the Rydberg structure from interactions between molecular core rotational motion and the orbital motion of the Rydberg electron in spite of the comparable classical time scales. In the present work, we investigate whether the additional structural and electrostatic complexity of a *molecular* solvent bound to a polyatomic molecule allows equally well-resolved high- n Rydberg structure and whether that structure shows any evidence of perturbations due to interactions between the degrees of freedom of the core and the Rydberg electron. We present here the first resolved high- n Rydberg spectrum of a van der Waals complex of a polyatomic molecule solvated by a diatomic molecule.

The experimental setup is essentially that described in detail elsewhere [15]: The outputs of two counterpropagating dye lasers interact with the output of a skimmed molecular beam deriving from a differentially pumped pulsed nozzle (General Valve, 300 μm orifice diameter).

All spectra presented here are one-photon resonant, two-color spectra obtained using the excimer pumped, frequency doubled output of one dye laser (Lambda-Physik FL 3002 using coumarin 153) and the undoubled output of a second probe laser (Radiant Narrowscan using coumarin 47). The Rydberg states are detected using the two complementary threshold ionization techniques of ZEKE and MATI spectroscopy, both of which were originally devised as high resolution variants of photoelectron spectroscopy. Both techniques rely on pulsed field ionization methods to sample states lying within $4.6\sqrt{V}$ cm^{-1} of the ionization threshold (this figure refers to diabatic ionization measured at the low wave number onset of field ionization [19]). Consequently, in ZEKE spectroscopy, which relies on the detection of electrons deriving from field ionization, the much smaller electric field strengths employed sample a very narrow cross section of Rydberg states lying within 1 to 2 cm^{-1} of each ionization threshold. The ZEKE spectra presented here were recorded using a combination of two pulses; the first ($+216$ mV cm^{-1}), applied about 1 μs after the laser shot, acts as a discrimination pulse to remove fast photoelectrons produced when the total photon energy exceeds the adiabatic ionization energy (as well as a cross section of the highest- n Rydberg states), while the second (-248 mV cm^{-1}), applied 200–300 ns later, acts as the main field ionization pulse. For the MATI experiments, which rely on the detection of ions, the lasers interact with the molecular beam about 1 cm upstream from the center of the ionization region: a single prepulse of 1.7 to 6.5 V cm^{-1} is then applied with a pulse width of 8 to 10 μs , prior to the subsequent application of the field ionization pulse (220 to 680 V cm^{-1}). DABCO vapor was seeded in 20% nitrogen (BOC Gases, Research Grade)/argon (BOC Gases, CP grade) at typical stagnation pressures of between 400–700 mbar. The sample reservoir, located immediately behind the nozzle, was heated to between 40 and 75 $^{\circ}\text{C}$. All quoted energies are corrected to vacuum.

DABCO (1,4-diazabicyclo[2.2.2]octane) is a bicyclic caged amine with D_{3h} symmetry whose lowest excited states arise from localized Rydberg transitions from the nitrogen lone-pair orbitals. In the nitrogen solvated complex, the ground state structure is influenced by quadrupole-quadrupole interactions and the nitrogen binds in an (offset) parallel configuration between two of the carbon bridges [20]. The resonance enhanced multiphoton ionization spectrum of the intermediate S_1 state of the complex shows a long progression in a van der Waals rocking mode, characterized in part on the basis of divergent vibrational energy level spacings [20]. The two-color ($1 + 1'$) MATI spectrum of DABCO- N_2 recorded via the first singlet excited state band origin ($S_1 0^0$) is compared to the analogous ZEKE spectrum in Fig. 1. The two spectra are essentially equivalent to each other, exhibiting course vibrational structure characteristic of

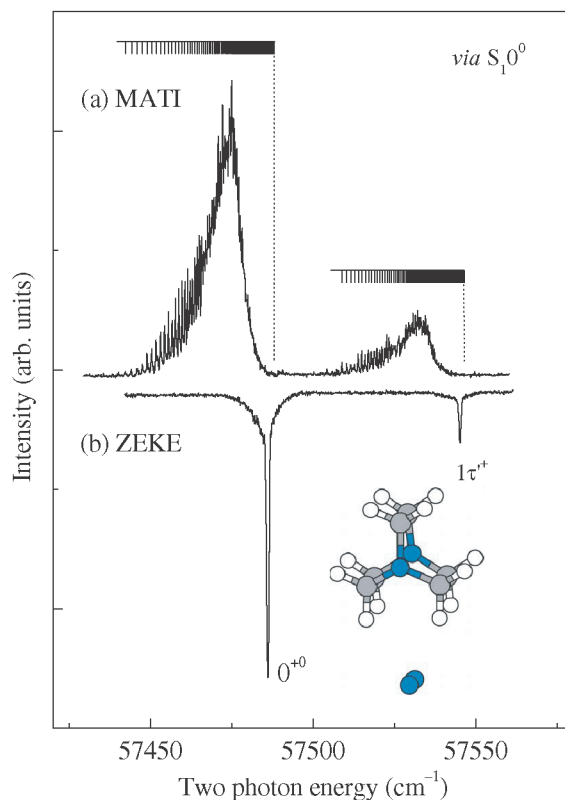


FIG. 1 (color online). A comparison of (a) the two-color ($1 + 1'$) MATI spectrum of DABCO- N_2 recorded via the $S_1 0^0$ band origin with (b) the analogous ZEKE spectrum. Each spectrum shows two bands, the first corresponding to the cation band origin ($\nu = 0$) and the second to the van der Waals mode fundamental (labeled $1\tau^+$). Each band in the MATI spectrum consists of a single resolved Rydberg series extending from $n = 49$ for the band origin and $n = 54$ for the $1\tau^+$ band.

the electronic ground state of the complex cation. The first and most intense band in each spectrum is assigned to the band origin and the second, weaker band which lies 59 cm^{-1} to higher energy, is assigned to one quantum excited in the van der Waals mode, labeled $1\tau^+$. However, the widely different field strengths result in dramatically different bandwidths between the two spectra: At the field strengths used in the ZEKE spectrum, field ionization onset occurs at around $n = 160$, with a maximum in ionization cross section occurring around $n = 185$ and then declining to zero at about $n = 205$; states lying above this point generally have reduced lifetimes because of their extreme sensitivity to stray fields and are not observed [7]. The resulting ZEKE bandwidth in this case is of the order of 1 cm^{-1} (FWHM) and allows resolution of the underlying rotational branch structure. The much higher field strengths employed in the MATI experiment (which relies on the detection of ions) sample states lying within 50 cm^{-1} of each threshold (extending down to about $n = 50$ in the experiments described here). As a result the MATI spectra have a bandwidth of about 15 cm^{-1} (FWHM), but more interestingly show the finely

resolved substructure of the Rydberg series converging to a given ionization threshold. A fit of the term values of the Rydberg series converging to the cation $v = 0$ level yielded an ionization energy of $57\,488.10 \pm 0.06 \text{ cm}^{-1}$. This value is about 2 cm^{-1} higher in energy than the analogous ZEKE band maximum and is consistent with the expected ionization energy redshift.

Figure 2 shows a comparison of the MATI and ZEKE spectra recorded via the $S_1 1\tau'$ intermediate state. These spectra demonstrate a classic Franck-Condon redistribution of vibrational energy into the $\Delta v = 0$ transition with weaker intensity in the off-diagonal components ($\Delta v = \pm 1$). Once again each vibrational band in the MATI spectrum exhibits dense Rydberg fine structure, although in this particular spectrum not as finely resolved as that in Fig. 1.

A high resolution scan of the $1\tau'^+$ band recorded via the $S_1 1\tau'$ intermediate state is shown in Fig. 3. The spectrum, which was recorded using a smaller separation field compared to that used for the other MATI spectra,

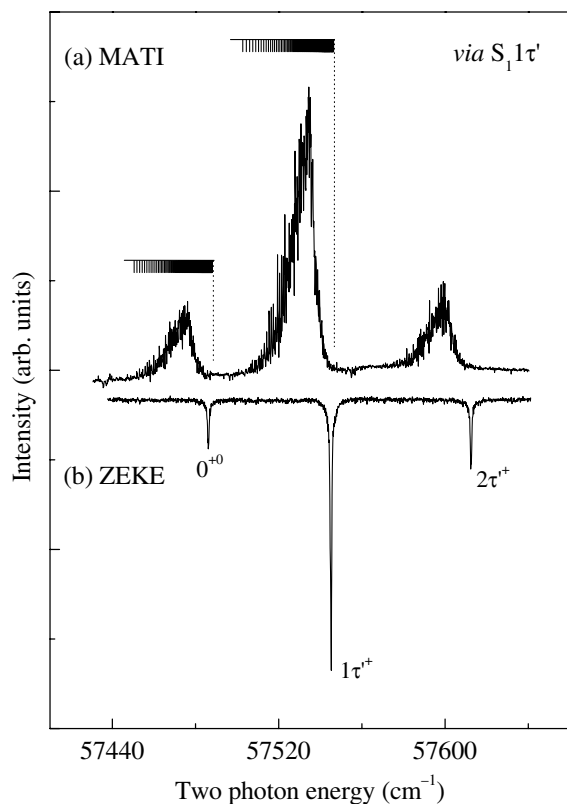


FIG. 2. A comparison of (a) the two-color ($1 + 1'$) MATI spectrum of DABCO- N_2 recorded via the $S_1 1\tau'$ intermediate state with (b) the analogous ZEKE spectrum. Each spectrum displays three bands corresponding to the cation band origin, the fundamental and the first overtone in the van der Waals mode. The Rydberg structure in this spectrum was less well resolved than in the other spectra and consequently no fits were obtained for the Rydberg series converging to the first overtone in the van der Waals mode ($2\tau'^+$).

shows a single Rydberg series with an onset at about $n = 58$ and is resolvable as far as $n = 96$. The maximum in ionization cross section occurs at about $n = 120$ and thereafter declines rapidly as the ionization threshold is approached. The loss in intensity beyond $n = 120$ is due to the prepulse used to separate the high- n Rydberg neutrals from prompt photoions prior to the application of the high voltage ionization pulse. The fact that any signal is seen at all implies that all of the resolved Rydberg states have lifetimes exceeding the $10 \mu\text{s}$ delay employed after the laser shot. The reason for this is that while the initial Rydberg state optically accessed by the probe laser will have orbital angular momentum values dictated by the optical selection rules, they rapidly acquire nonpenetrating high- ℓ high- m_ℓ character through the effects of small homogeneous fields (Stark mixing) and inhomogeneous electric fields (associated with regions of localized charge in the spectrometer). Fitting the term values to the Rydberg formula yields an ionization energy of $57\,546.45 \pm 0.04 \text{ cm}^{-1}$ and a quantum defect of $\delta = -0.089 \pm 0.06$, which suggests an assignment to an nd or nf series or conceivably to an ns series with near-integral quantum defect. The observation of a series with a vanishing quantum defect implies either that states initially accessed by the optical transition have intrinsically high- ℓ character or that they rapidly acquire nonpenetrating character within a time frame that limits nonradiative decay. Nevertheless, the decline in intensity to the lower energy side of the band maximum reflects the increasing sensitivity of the lower- n states to decay processes, due to interactions with the core. There does appear to be some reduction in linewidth with increasing n , when comparing lines at the onset of the band with those in the region of $n = 90$. However, it is unclear from the spectrum whether this n dependence is maintained as the line spacings approach the laser linewidth, because we are unable to fully resolve the complete line profile beyond about $n = 68$. Although the line positions of the Rydberg series are largely unperturbed (within the limits of our spectral resolution), it is noticeable that the intensity does fluctuate somewhat, with a number of negative dips in intensity observable throughout the spectrum. The most likely explanation for this is the presence of lower- n ($33 \leq n \leq 39$) core-excited Rydberg states in this region, converging to the $2\tau'^+$ band: the loss of intensity at these positions would then be due to a mixing of the much shorter lifetime $2\tau'^+$ Rydberg states with the metastable $1\tau'^+$ states, which then do not survive the $10 \mu\text{s}$ delay.

For any molecular complex Rydberg state, the center of charge will be located on the component having the lower ionization energy, which in this case is the DABCO chromophore. Rotation of the charge center about the center of mass thus resembles an oscillating dipole with a dipole moment considerably larger than that of neutral polar molecules. Similarly, excitation of a van der Waals intermolecular mode leads to a periodically changing

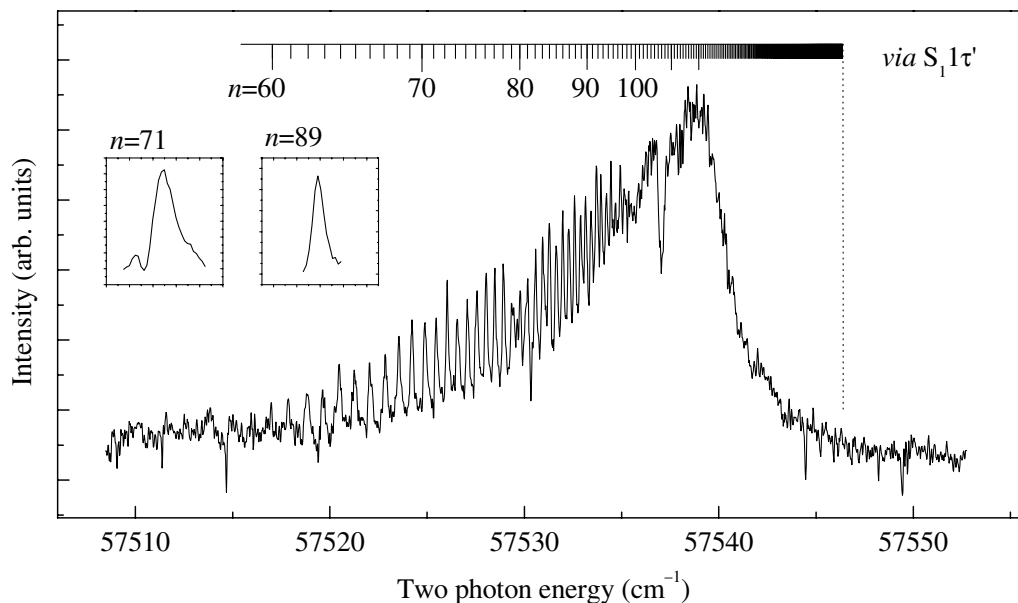


FIG. 3. A high resolution scan of the $1\tau^+$ MATI band recorded via the $S_11\tau'$ intermediate state. The spectrum shows a single Rydberg series with an onset at about $n = 58$ and resolvable as far as $n = 96$. The lower separation field used in this case has resulted in a very well-resolved Rydberg series extending over a much larger range of principal quantum number than in the other MATI spectra (which start lower but do not extend to such high values of n).

dipole albeit oscillating on a time scale somewhat shorter than rotation. In either case, it is not unreasonable to expect some evidence of perturbation to the observed Rydberg series from coupling of the rotational (and/or vibrational) motions with the electronic motion [21]. Furthermore, the complex studied here is bound to some extent by interactions between the quadrupoles of both components which adds a further potential source of perturbation. However, the observation of clearly resolved and apparently unperturbed Rydberg series progressions converging to each vibronic threshold in DABCO- N_2 suggests that even for large polar molecular cores bound by a complex mixture of dispersion, charge and quadrupole-quadrupole interactions, the interaction between the Rydberg electron and core in the region of the ionization threshold remains very weak.

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