which was taken into account in the earlier computations.[1] A convenient RRKM formula making provision for the barrier has been given by Troe.[8] Inspection of it shows that the barrier has the effect of multiplying (7) on the right hand side by the correction factor

$$F(\text{barrier}) = \frac{2.15(E_0/kT)^{1/3}}{2.15(E_0/kT)^{1/3} - 1 + (E_0 + E_z)/tkT} , \qquad (8)$$

where t is s for a linear complex and is $s + \frac{1}{2}$ for a nonlinear complex. In the range 80–300 °K this factor is approximately proportional to $T^{1/2}$ so that its introduction eliminates the unacceptable discrepancy to which attention was drawn in the preceding paragraph. Its magnitude is less than unity. In cases where neither reactant is polyatomic the modified theoretical results (with the anharmonicity enhancement[8] included) are significantly lower than suggested by experiment. This may be due to the complex having free internal rotations as postulated in the original model.[1] The effect of f such rotations is to multiply the right hand side of (7) by the further factor[7]

$$F(\text{free}) = \frac{(s-1)!}{(s + \frac{1}{2}f - 1)!} \left(\frac{E_0 + E_z}{kT}\right)^{f/2} q(\text{rot})^f , \qquad (9)$$

$q(\text{rot})^f$ being their partition function. As an example it is sufficient to mention

$$N_2^+ + N_2 + He \rightarrow N_4^+ + He \ . \qquad (10)$$

Adams *et al.*[9] have carried out the most recent measurements. They found the rate coefficient at 114 °K to be as great as 6.6×10^{-28} cm^6 sec^{-1}. This value cannot be attained if free internal rotations are ignored but can be if four of them are assumed and (9) is used with $q(\text{rot})^f$ as for the isolated reactants.[10]

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Intramolecular dynamics of an isolated ultracold large molecule

A. Amirav, U. Even, and Joshua Jortner

Department of Chemistry, Tel-Aviv University, Tel Aviv, Israel

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Intramolecular, nonreactive, radiationless processes in electronically–vibrationally excited states of collision-free "isolated" large molecules involve interstate electronic relaxation (ER)[1] and intrastate vibrational energy redistribution (IVR).[2] Interrogation of the excited-state population following photoselective excitation of isolated, large molecules at room temperature[3] is hampered by thermal inhomogeneous broadening (TIB) effects, originating from rotational broadening as well as from severe vibrational sequence congestion. These effects of TIB can be circumvented by the use of supersonic-free expansion in seeded beams,[4] which result in ultracold isolated large molecules, whose excited-state energetics[5] and lifetimes[6] can be studied. We wish to report some novel features of excited-state dynamics of isolated, ultracold, large aromatic molecules. We have studied the energetics and intramolecular dynamics in the first electronically excited singlet $S_1(^1B_{2u})$ state of tetracene and pentacene seeded in a supersonic molecular beam of Ar and of Kr. The lifetimes, τ, of photoselected states at excess vibrational energy $E_v = 0$–4000 cm^{-1} drastically differ, in respect with their absolute values as well as their E_v dependence, from the lifetimes obtained from low-pressure bulb experiments at room temperature.[7] The experimental data for intramolecular dynamics in the S_1 state of ultracold tetracene ($C_{18}H_{12}$) reported herein demonstrate the following:

(1) Meaningful information concerning the E_v dependence of ER and IVR in large isolated molecules can be obtained only when TIB effects are eliminated.

(2) The details of the current theory of optical selection in ER[8,9] require gross modification.

(3) Novel information regarding IVR can be obtained from studies of ultracold molecules.

We have found that the degree of rotational and vibrational cooling of several molecules (I_2, CrO_2Cl_2, $C_{18}H_{12}$) seeded in supersonic jets of Ar and Kr was much more efficient than in He. The supersonic expansion of tetracene (heated in the sample chamber to ~220 °C) in Ar and Kr was conducted through a nozzle with a diameter $d = 160$ μm, the backing pressure being $p = 150$ Torr. The low values of p^2d under our experimental conditions markedly decrease the probability of formation of van der Waals complexes between tetracene and the rare-

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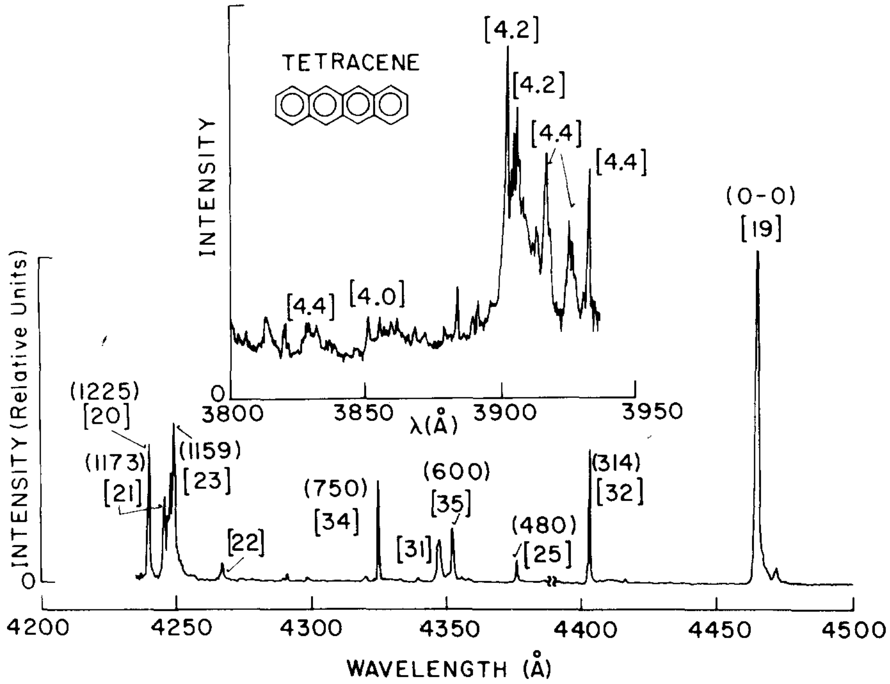

FIG. 1. Fluorescence excitation spectrum of gas phase isolated tetracene cooled in a supersonic expansion. Tetracene was seeded into Ar and expanded from a pressure of 150 Torr through a 150 μm nozzle. The exciting dye laser had a bandwidth of 0.3 cm^{-1}. All the fluorescence excitation spectra are normalized to the laser intensity. The fluorescence intensity in the region 4235–4385 Å should be scaled by ($\frac{1}{4}$) relative to the range 4400–4500 Å. The origin is labelled as (0–0). Numbers in round brackets ( ) denote frequencies of several fundamental vibrations (in cm^{-1}). Numbers in square brackets [ ] denote fluorescence decay lifetimes (in nsec).

gas atoms. The pulsed nitrogen-pumped dye laser (Molectron DI2) with spectral bandwidth of 0.30 cm^{-1} and pulse width (HWHM of 3 nsec crossed the supersonic beam at 7 mm down the nozzle. The fluorescence was collected through a light pipe and detected by a photomultiplier (Hammamatso 936). The fluorescence excitation spectrum was recorded by a boxcar integrator after normalization to the laser intensity. Lifetimes were measured by a Biomation transient recorder (model 1800) and were averaged by a home-built signal averager.

The fluorescence excitation spectrum of tetracene in the regions 4200–4500 Å (region A) and 3800–3950 Å (region B) are shown in Fig. 1. No fluorescence excitation could be detected at energies below 22 300 cm^{-1}. We have demonstrated that the spectrum originates from the molecule rather than from van der Waals complexes on the basis of the following evidence: (a) We have conducted a careful comparison between the spectra in Ar and in Kr at 150–200 Torr. The spectra were practically identical. (b) Changing the downstream temperature by varying the Ar pressure in the range 20–150 Torr resulted only in rotational broadening, and in the appearance of hot and sequence vibrational bands with increasing temperature, while other spectral features were not changed. (c) Only at higher Ar and Kr pressures ($p = 200$–800 Torr) were new features attributed to complexes observed.

The electronic origin for the $S_0(^1A_{1g}) \to S_1(^1B_{2u})$ transition is assigned to be located at 4469.7 Å (22 373 cm^{-1}). Eleven fundamental vibrations of tetracene were identified (seven of which are shown in Fig. 1), being in good agreement with mixed crystal[10(a)] and Raman[10(b)] data.. Individual spectral features in region A have a width of ~3 cm^{-1}, presumably due to unresolved rotational structure. Region A exhibits well separated individual vibronic bands. In this energy region the vibrational level structure in the S_1 manifold is sparse. With increasing E_v Fermi resonances are exhibited, e.g., the three bands in the vicinity of 4250 Å. In the higher energy region B the spectrum of the ultracold molecule exhibits overlapping bands superimposed on a background. This congested level structure corresponds to overlapping resonances, originating from many-level Fermi resonances, provides the spectroscopic manifestation of intrastate IVR.

The time-resolved fluorescence decay following photoselective excitation (bandwidth 0.3 cm^{-1}) exhibited a single exponential decay mode. Some lifetimes are summarized in Fig. 1. The lifetime $\tau = 19$ nsec at the electronic origin of the ultracold molecule is considerably longer than the 5–6 nsec lifetime measured at 4469.7 Å for the thermally broadened absorption band of tetracene in 20 Torr Ar. The latter value concurs with previous results for the isolated molecule at 210 °C.[7] Thus, many features of ER cannot be unveiled at room temperature. Excitation of the low frequency 314, 480, 600, and 750 cm^{-1} fundamentals results in a surprising retardation of the ER rate relative to the ER at the origin, the decay lifetimes being close to the pure radiative lifetime, $\tau_R = 30$ nsec in solution.[11] ER from the S_1 manifold can occur via two channels: $S_1 \to T_1$ and $S_1 \to S_0$. The blocking of the ER rate in region A is in contrast with most theoretical predictions,[8,9] which envision decrease of τ with increasing E_v and can be reconciled with available theories only provided the $S_1 \to T_1$ channel dominates with the $S_1 - T_1$ energy gap being low.[8] With increasing E_v beyond region A, τ decreases with increasing E_v until in region B, where $E_v = 2000$–3800 cm^{-1}, τ is practically constant. The independence (or the very weak dependence) of the ER decay rate on E_v in region B can be reconciled in terms of $S_1 \to S_0$ ER, where the effects of IVR within the (vibrationally excited) S_1 manifold result in efficient intrastate anharmonic scrambling, which is in accord with the spectroscopic data in this high-energy region.

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NOTES

Unrestricted Hartree–Fock (UHF) calculations of singlet and triplet diradicals: Nitrene peroxide (HNOO)[a]

Kizashi Yamaguchi, Satoshi Yabushita, and Takayuki Fueno

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

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The restricted Hartree–Fock (RHF) molecular orbital (MO) method fails to interpret the electronic properties of singlet diradicals in both the qualitative and quantitative sense.[1] Because of this deficiency of the method it has been emphasized that the MO method is not applicable to unstable molecules.[2] However the singlet RHF (^{1}RHF) solution itself is not a stable and true HF solution for singlet diradicals, involving various instabilities which predict the appearances of the more general HF (GHF) solutions.[1,3] Indeed the bond-alternating (complex charge density wave)[4a] and spin density wave (SDW)[4b] solutions are more stable than the ^{1}RHF in the case of typical antiaromatic 4π electron systems.[1(b)] In the present paper we wish to show that the eight different diradical states of nitrene peroxide (HNOO) are well described by the SDW solutions which are equivalent to the unrestricted HF (UHF) solutions[5] in this case. The species is isoelectronic to ozone[6] (O_3) and methylene peroxide[7] (CH_2OO), being of special interest in relation to the generalized VB (GVB) descriptions of O_3 and CH_2OO by Goddard *et al.*[2]

The geometry of nitrene peroxide examined is illustrated by A of Fig. 1. Calculations were carried out using the *ab initio* DZ (431G) basis.[8] The ^{1}RHF solution of HNOO involves the triplet instability[1,4] arising from the π–π triplet excitation, being reorganized into the more stable singlet UHF (^{1}UHF) solution which is responsible for the singlet (π, π)-diradical state.[1] Indeed the ^{1}UHF HOMO's obtained are essentially localized on

TABLE I. The energies and orbital spin densities (ρ) on the N and terminal O atoms for eight diradical states of HNOO.

		ρ(N)				ρ(O)			
Type	Energy (eV)	s	x	y	z	s	x	y	z
$1_{\pi\pi}$	0.0[a]	−0.07	−0.07	−0.01	−0.94	0.02	0.02	0.10	0.90
$3_{\pi\pi}$	0.076	0.08	−0.02	0.05	0.95	0.02	0.00	0.09	0.92
$3_{\pi\sigma}$	0.592	0.06	0.11	0.11	0.93	0.02	0.86	0.19	0.00
$1_{\pi\sigma}$	0.647	−0.08	0.04	−0.02	−0.92	0.02	0.87	0.22	−0.00
$3_{\sigma\pi}$	2.975	0.16	0.12	0.55	0.01	0.01	0.10	0.11	0.85
$1_{\sigma\pi}$	3.115	−0.17	−0.15	−0.56	0.01	0.03	0.06	0.03	0.85
$1_{\sigma\sigma}$	3.976	−0.17	−0.10	−0.54	−0.00	0.03	0.79	0.13	−0.00
$3_{\sigma\sigma}$	4.016	0.18	0.18	0.55	−0.00	0.01	0.84	0.32	0.00

[a] $E_{total} = -204.2353$ a.u.

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