(s, 3 H), 1.20 (d, *J* = 7.5 Hz, 3 H), 3.31 (q, *J* = 7.5 Hz, 1 H), 3.34 (s, 3 H), 3.40 (s, 3 H), 6.00 (br, 2 H, NH_2), 7.11 (s, 1 H). (*E*)-**4a:** syrup; ^1H NMR (CCl_4) δ 0.96 (t, *J* = 6.5 Hz, 3 H), 1.16–1.74 (m, 4 H), 2.36 (t, *J* = 7 Hz, 2 H), 3.25 (s, 3 H), 3.46 (s, 3 H), 6.95 (br s, 1 H), 8.23 (s, 1 H); UV (CH_3CN) 313 nm (log ϵ 4.05), 259 (3.92). (*Z*)-**4a:** syrup; ^1H NMR (CCl_4) δ 0.95 (t, *J* = 6.6 Hz, 3 H), 1.22–1.76 (m, 4 H), 2.32 (t, *J* = 7 Hz, 2 H), 3.25 (s, 3 H), 3.42 (s, 3 H), 6.86 (br s, 1 H), 7.44 (s, 1 H); UV (CH_3CN) 303 nm (log ϵ 4.02), 258 (3.79). **4b:** syrup; ^1H NMR ($CDCl_3$) δ 1.33 (t, *J* = 7 Hz, 3 H), 1.76 (s, 3 H), 1.98 (s, 3 H), 1.60–2.10 (m, 4 H), 2.46 (s, 3 H), 2.75 (t, *J* = 7 Hz, 2 H), 3.65–3.80 (m, 1 H), 3.76 (d, *J* = 1 Hz, 2 H), 4.18–4.26 (m, 1 H), 4.38 (dd, *J* = 6, 2 Hz, 1 H), 5.30 (d, *J* = 2 Hz, 1 H), 6.42 (s, 1 H), 7.76 (s, 1 H), 9.50 (br, 1 H, NH); judging from the chemical shifts of the olefinic (δ 6.42) and C-6 (δ 7.76) protons, **4b** appears to be *Z* isomer. **6:** viscous oil; ^1H NMR ($CDCl_3$) δ 1.80–2.18. (m, 6 H), 3.08–3.22 (m, 1 H), 3.36 (s, 3 H), 3.42 (s, 3 H), 3.5–3.6 (m, 1 H), 7.15 (s, 1 H). **8:** mp 119–120 °C; ^1H NMR ($CDCl_3$) δ 1.10 (s, 3 H), 1.15 (s, 3 H), 1.21 (d, *J* = 7 Hz, 3 H), 2.28 (q, *J* = 7 Hz, 1 H), 3.36 (s, 3 H), 3.82 (s, 3 H), 9.90 (br s, 1 H, NH); UV (CH_3CN) 306 nm (log ϵ 3.88). **10:** mp 107–108 °C; ^1H NMR ($CDCl_3$) δ 1.40–2.10 (m, 6 H), 2.80–3.20 (m, 1 H), 3.38 (s, 3 H), 3.66 (s, 3 H), 3.40–3.60 (m, partially obscured, 1 H); UV (CH_3CN) 313 nm (log ϵ 3.82), 249 (3.27). **11:** viscous oil; ^1H NMR ($CDCl_3$) δ 1.30–2.20 (m, 12 H), 2.90–3.30 (m, 2 H), 3.30 (s, 3 H), 3.36 (s, 3 H), 7.06 (s, 1 H). **13:** viscous oil; ^1H NMR (CCl_4) δ 0.95 (t, *J* = 6 Hz, 3 H), 1.20–1.80 (m, 6 H), 2.12–3.00 (m, 3 H), 3.24 (s, 3 H), 3.36 (s, 3 H), 7.24 (s, 1 H). **15;** viscous oil; ^1H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 2.95 (d, *J* = 7 Hz, 2 H), 3.35 (s, 3 H), 3.42 (s, 3 H), 5.58 (t, *J* = 7 Hz, 1 H), 7.26 (s, 1 H).

(11) Both isomers of **4a** are interconvertible under the irradiation conditions.

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(13) A considerable amount of polymeric products derived from the olefin and 1-hexyne has been detected. In the absence of olefins **1a** undergoes photodimerization.

(14) A mixture of two stereoisomers. The major isomer was isolated in a pure crystalline form: mp 89–90 °C; ^1H NMR ($CDCl_3$) δ 1.60–2.20 (m, 6 H), 2.80–3.20 (m, 2 H), 3.08 (d, *J* = 6 Hz, 1 H), 3.02 (s, 3 H), 3.22 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 24.3, 27.4, 28.8, 30.5, 31.6, 41.8, 41.9, 47.5, 53.1, 114.9, 150.8, 166.5; IR (Nujol) 1710, 1660 cm^{-1}. This compound did not epimerize upon prolonged exposure to basic alumina, suggesting that the 6–4 ring fusion is cis.[15] Attempts to purify the minor isomer have been unsuccessful.

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(17) Irradiation was done with a 450-W high pressure Hg lamp at 20 °C through a 0.4 M stannous chloride filter solution (cutoff 320 nm).[5b] Under these conditions >95% of the incident light was absorbed by the sensitizer.

(18) Alternative mechanism involving a carbene intermediate derived from **18** appears to be less likely since alcohols should trap such intermediates. In support of the proposed mechanism, irradiation of 5-deuterated **1a**[9b] (90% D) with cyclopentene (3 equiv mol) in $CHCl_3$ provided the 6-deuterio derivative of **6** (55% D). However, a considerable amount of the deuterium of **1a**-d_1 was lost during the photoaddition. Mechanistic studies including trapping experiments of the intermediate are in progress.

(19) The mechanism of the formation of **9** is not clear at this time. Other interpretations are certainly possible.

(20) Conformational change of the biradical **17** by increasing temperature is possibly responsible for this process. A similar temperature-dependent photorearrangement has been observed with geranonitrile; see ref 16b.

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Isao Saito,* Koji Shimozono, Teruo Matsuura*
Department of Synthetic Chemistry
Faculty of Engineering, Kyoto University
Kyoto 606, Japan

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Two-Laser Multiphoton Dissociation of Iodobenzene Cation

Sir:

The simultaneous irradiation of gas-phase iodobenzene ions with 610-nm visible light and 10-μ infrared light results in photodissociation of the ions at a rate strikingly faster than the photodissociation observed with either laser used separately. This simultaneous visible-infrared process has important implications for the nature of multiphoton events and relaxation processes in gas-phase species, and may represent the first observation of a combined visible-IR multiphoton dissociation.

Gas-phase ionic molecules offer a uniquely attractive opportunity for study of multiphoton photochemistry, because of the ease of trapping ions under collision-free or collisional conditions for periods of many seconds or longer. The Penning ion trap with ion cyclotron resonance detection has proven to be a powerful approach to exploiting these possibilities.[1,2]

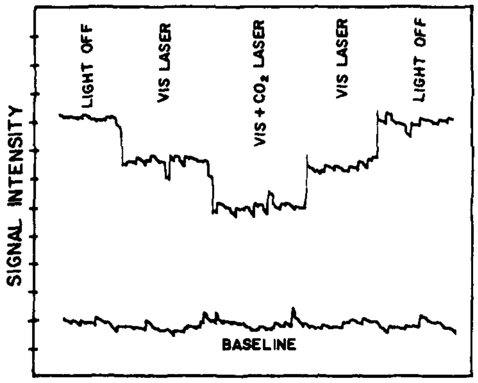

Figure 1. Recorder trace of the pulsed-ICR-detected parent-ion abundance. The time between ion formation and ICR detection is 2.0 s, during which period the ions are irradiated by no light, by either laser alone, or by both lasers, as indicated.

Two notable types of multiphoton processes have been studied for ions: the sequential two-photon (and multiphoton) photodissociation of cations at visible wavelengths with light sources of modest power,[3-5] and multiphoton infrared photodissociation of ions using CW CO_2[2,6,7] lasers. The two-photon visible-wavelength photodissociation of iodobenzene radical cation has been previously described.[8] In the work reported here, visible irradiation was provided by a Chromatix pulsed dye laser operated at 610 nm (which is near the two-photon peak) and at pulse rates between 5 and 30 pulses/s.[9] Dissociation using only the visible laser shows characteristics of pressure dependence and light-intensity dependence consistent with the accepted sequential two-photon dissociation model.

Used alone, the CO_2 laser (unfocussed CW, up to ~10-W/cm^2 power) gave no observable dissociation, but the combination of visible and IR irradiation gave the greatly enhanced dissociation shown in Figure 1. The wavelength dependence of the IR enhancement in the 10-μ region of visible two-photon photodissociation is shown in Figure 2. IR irradiation in the region around 9.6 μ gave little or no enhancement, so that the IR wavelength dependence evidently reflects a broad maximum at ~10.2 μ. Such a broad IR peak, lying in a spectral region where iodobenzene neutral has several absorption peaks, is consistent with IR absorption by a vibrationally excited iodobenzene ion.[10]

At fixed IR intensity, the visible intensity dependence of photodissociation is somewhat stronger than linear, but much weaker than quadratic. The IR intensity dependence is weaker than linear as shown in Figure 2. The pressure dependence is strong at low pressure, but becomes weaker at high pressure (the extent of dissociation decreasing with increasing pressure).

We believe these observations can be understood by considering the behavior of an ion under IR irradiation at modest power: the absorption of IR photons into the resonant normal mode, pumping the ion to higher vibrational energy, is balanced by energy relaxation by collision and by IR radiation. The relevant characteristics of all three of these processes are known or can be estimated,[11-13] and modeling indicates that a balance is rapidly established between excitation and relaxation such that the ion is maintained within a reasonably narrow energy range. It has little chance of falling back near the ground state and has also little chance of exceeding a characteristic maximum energy which increases with increasing IR intensity.[14] Such IR pumping has a marked effect on the two-photon photodissociation process: when an ion

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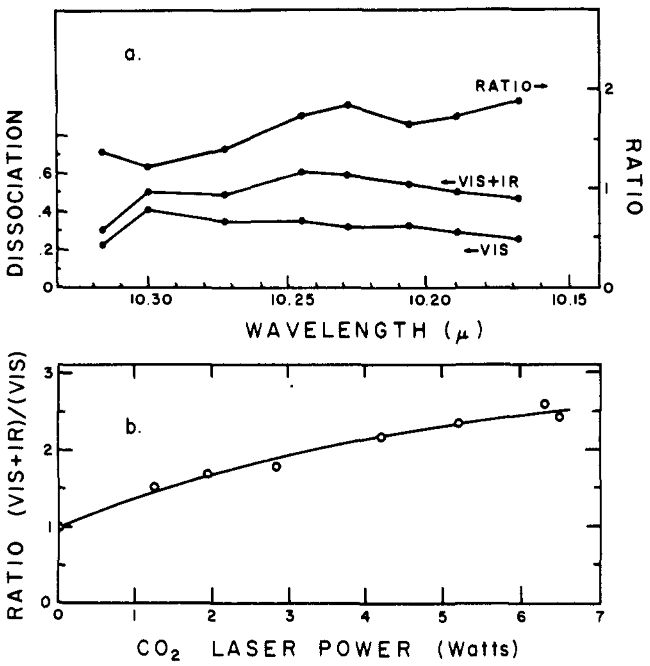

Figure 2. (a) Wavelength dependence of photodissociation. The lower two plots are the dissociation ($-\ln P/P_0$, where P and P_0 are the parent ion signals, respectively, with and without light) for visible light only and for combined visible and IR irradiation (left-hand scale). The upper plot (right-hand scale) is the ratio of these (pressure 1.5×10^{-7} Torr). (b) Plot of the ratio of two-laser photodissociation to visible-laser-only dissociation as a function of IR laser power (pressure 5×10^{-8} Torr).

absorbs the first visible photon to put it 2 eV or more above the ground state, the IR pumping slows its subsequent relaxation and maintains it in the region of pumping/relaxation balance.[15] The probability of the ion remaining excited long enough for absorption of another visible photon is thus greatly increased, enhancing the dissociation rate.

Quantitative computer modeling of the two-laser photodissociation process suggests that the pressure dependence, visible intensity dependence, visible pulse rate dependence, and IR intensity dependence can be successfully accounted for within this model. These comparisons will be described in a fuller publication. The kinetic model applied here, involving sequential photon absorption and stochastic relaxation, is not fundamentally new, being a variety of the master-equation formalism.[16,17] However, it seems useful to point out that, at modest IR light intensities, this model leads to a (markedly non-Boltzmann) population of ions in dynamic equilibrium in an energy region part way between the ground state and the dissociation threshold.

The implications of this experiment for study of the properties of vibrationally excited species and vibrational relaxation processes are interesting. Steady low-level IR pumping of species like $C_6H_5I^+$ results in a stable steady-state population of ions with large and fairly uniform vibrational excitation. Two-photon visible photodissociation provides a successful probe for exploring some of the characteristics and dynamic behavior of these vibrationally excited ions. We are pursuing this approach in more depth and for other ions.

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(9) At low pressures, where the pulse rate is much faster than the collisional relaxation rate, this should be fully equivalent to using a continuous laser as in previous work, since the ion averages out the energy input of many laser pulses between collisions assuming the sequential photodissociation mechanism of ref 3-5. At high pressures, when relaxation of excited ions between pulses is appreciable, pulsed-laser excitation differs from CW excitation: this point will be treated in detail in a forthcoming publication.
(10) For illustration of excited-molecule IR absorptions, see Bloembergen, N.; Yablonovitch, E. *Phys. Today* **1978**, *31*, No. 5, 23.
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(14) Presumably the IR photodissociation of ions observed by Beauchamp et al.[2,6] occurs when this characteristic excitation energy is near or above the dissociation threshold, but in the present experiment it apparently lies well below the dissociation threshold (3 eV) even at the highest IR power used, since little or no dissociation is observed with the IR laser alone.
(15) It seems likely that some ions will occupy this energy region even in the absence of visible light. However, ions within ~0.3 eV of the ground state lie below the "quasi-continuum" and are expected to be pumped relatively slowly by IR radiation, so that visible light may well be necessary to prevent a substantial population from remaining near the ground state.
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Robert C. Dunbar,* John D. Hays
Jeffrey P. Honovich, Naomi B. Lev
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

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Exceptional Reactivity of the Bicyclo[2.2.1]heptene Double Bond

Sir:

Norbornene shows two exceptional characteristics in its reactivity: high preference for exo reaction and increased rate constants in all addition reactions including cycloadditions.

The exo selection was ascribed to a favorable transition state conformation (torsional effect)[1] or to a steric hindrance of endo attack.[2] The size of exo/endo ratios render both explanations doubtful. Inagaki, Fujimoto, and Fukui[3] applied the "orbital mixing rule" to norbornene and deduced "nonequivalent orbital extension", i.e., greater exo than endo lobes for the π HO; this change of hybridization (see formula **1**) was made responsible for preferential exo addition of electrophilic reagents.[3]

The increased reactivity of norbornene as a dienophile or dipolarophile compared with simple cycloalkenes was interpreted by the release of ring strain in the transition state.[4] The heat of hydrogenation of norbornene exceeds that of cyclohexene by 6 kcal mol^{-1}.[5] The 1,3-dipolar cycloadditions of benzonitrile oxide,[6] diazomethane,[7] and phenyl azide[8] to norbornene are 6100-, 5400-, and 5700-fold faster than those to cyclohexene, corresponding to $\Delta\Delta G^{\ddagger} = 4.7$-$5.1$ kcal mol^{-1}. On the other hand, in the last decade evidence for *early* transition states of concerted cycloadditions has accumulated,[9-11] i.e., only a fraction of the 6 kcal mol^{-1} (roughly the difference between the strain energies of norbornene and norbornane) can be released in the transition state.

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