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# Vacuum ultraviolet absorption spectroscopy in supersonic expansions

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Remarkable progress has been accomplished in the area of molecular spectroscopy in supersonic expansions, which unveiled many facets of excited-state energetics and dynamics of large molecules excited in the energy range 0.2–6 eV.<sup>1–4</sup> Photosensitive molecular excitation in jets above 6 eV is expected to open new horizons in the areas of extravalence spectroscopy, nonreactive and reactive intramolecular dynamics, and state selective molecular photochemistry.<sup>5</sup> A significant step in this direction was undertaken recently by three- and four-photon ionization studies<sup>6–9</sup> in jets and by femtosecond time-resolved investigations<sup>10</sup> of Rydberg states. We wish to report on the merger between the techniques of vacuum ultraviolet (VUV) spectroscopy and supersonic jets, which allows for the interrogation of absorption spectra of large molecules in supersonic expansions in the near VUV (6–9 eV) region. The techniques of absorption spectroscopy in seeded, planar, pulsed, supersonic expansions<sup>11–13</sup> were adopted for VUV absorption studies. Planar supersonic jets of Ar seeded with benzene, benzene-D<sub>6</sub> or naphthalene were expanded from a nozzle slit (dimensions 0.27 × 90 mm, repetition rate 9 Hz and gas pulse duration 300 μs) and the characteristic rotational temperatures were  $T_R \approx 20$  K. Light (spectral range 1500–2000 Å) from a modified short-arc high-pressure Xe lamp (EG & G Model FX 193U), which was fitted with a sapphire or CaF<sub>2</sub> window, was focused with an  $f = 4$  CaF<sub>2</sub> lens onto the jet parallel to the nozzle slit at a distance  $x = 8$  mm. The light beam was split by a CaF<sub>2</sub> plate and monitored by two photomultipliers coated with a (tetraphenyl butadiene) convector, both before and after crossing the planar jet. The absorption  $\Delta I/I_0$  was normalized to the incident light intensity.

VUV absorption spectra of jet-cooled aromatic molecules provided information on intramolecular dynamics of odd-parity Rydberg states and an interference between Rydberg and intravalence excitations. The electronic origin of the  $3P_{x,y}(^1A_{2u})$  Rydberg excitation [ $3P_{x,y}(0)$ ] of benzene and

of benzene-D<sub>6</sub> (Fig. 1) is superimposed on the  $^1A_{1g} \rightarrow ^1E_{1u}$  intravalence transition.<sup>14,15</sup> The energy of  $3P_{x,y}(0)$  (55 877 cm<sup>-1</sup> for C<sub>6</sub>H<sub>6</sub> and 55 946 cm<sup>-1</sup> for C<sub>6</sub>D<sub>6</sub>) is in accord with one-<sup>14,15</sup> and three-photon<sup>16</sup> bulb spectroscopy. The line shape of  $3P_{x,y}(0)$  is a Lorentzian (Fig. 1) with a width (FWHM) of  $\Delta = 32.7 \pm 3.1$  cm<sup>-1</sup> for C<sub>6</sub>H<sub>6</sub> and  $\Delta = 29.0 \pm 2.0$  cm<sup>-1</sup> for C<sub>6</sub>D<sub>6</sub>. The homogeneous line-widths  $\Gamma$  and lifetimes  $\tau$  obtained after correction for instrumental resolution are  $\Gamma = 28 \pm 3$  cm<sup>-1</sup> ( $\tau = 0.19 \pm 0.02$  ps) for C<sub>6</sub>H<sub>6</sub>, and  $\Gamma = 24 \pm 2$  cm<sup>-1</sup> ( $\tau = 0.22 \pm 0.02$  ps) for C<sub>6</sub>D<sub>6</sub>. Our value  $pf\Gamma$  for  $3P_{x,y}(0)$  is close to the linewidths of 27–33 cm<sup>-1</sup> reported<sup>6</sup> for the vibronically induced two-photon transitions of this Rydberg transition. A small (~10%) normal deuterium isotope effect on the relaxation rate may exist, which is, however, within our experimental uncertainty, implying that the electronic relaxation process of  $3P_{x,y}(0)$  is characterized by moderate energy gap(s). The homogeneous line broadening of the  $^1A_{1g} \rightarrow ^1E_{1u}$  intravalence excitation of jet-cooled benzene exceeds  $\Gamma$  for  $3P_{x,y}(0)$  by about one to two orders of magnitude, which is in accord with old arguments,<sup>17</sup> so that the intramolecular relaxation of the intravalence  $^1E_{1u}$  excitation presumably occurs within ~10 fs, i.e., on a time scale comparable with a vibrational period. The Lorentzian line shape of  $^1A_{1g} \rightarrow 3P_{x,y}(0)$  provides compelling evidence for the absence of Rydberg-intravalence interference effects<sup>15,18,19</sup> in benzene, which is in accord with Rice *et al.*<sup>15</sup> The absence of Fano interference effects<sup>20</sup> can be rationalized within the framework of a random coupling model<sup>21,22</sup> for the  $3P_{x,y}(0) \rightarrow ^1E_{1u}$  interstate coupling terms and for the  $^1A_{1g} \rightarrow ^1E_{1u}$  transition moments to the homogeneously broadened background manifold, which erode all interference effects.<sup>21,22</sup> Pronounced Rydberg-intravalence interference effects<sup>18</sup> are exhibited in the spectrum of jet-cooled naphthalene (Fig. 2). The excessive line broadening of the resonance, e.g.,  $\Gamma = 80$  cm<sup>-1</sup> ( $\tau = 70$  fs) for the  $R_c^5 + 1360$  transition (Fig. 2), is close to the corresponding

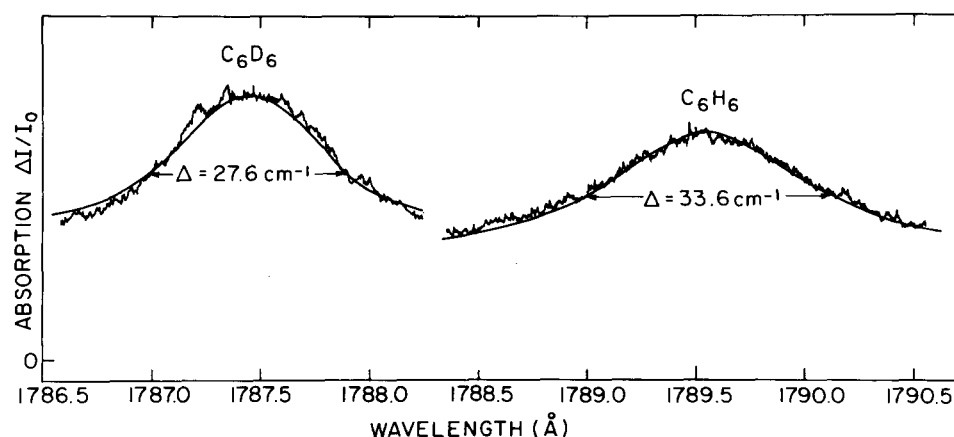


FIG. 1. Absorption spectra of the  $^1A_{1g} \rightarrow 3P_{x,y}(^1A_{2u})$  electronic origin of benzene and benzene-D<sub>6</sub> in pulsed planar supersonic expansions of Ar at  $p = 105$  Torr. The spectral resolution is 0.45 Å. The base line is marked as zero on the intensity scale. The solid curves represent fits of the line shape  $L(\lambda)$  to a Lorentzian superimposed on a constant background  $L(\lambda) = A + C/[(\lambda - \lambda_0)^2 + (\Delta/2)^2]$ . For C<sub>6</sub>H<sub>6</sub>:  $A = 5.7$ ,  $C = 17.2$  (in arbitrary units),  $\lambda_0 = 1789.65$  Å and  $\Delta = 1.08$  Å (33.7 cm<sup>-1</sup>) while for C<sub>6</sub>D<sub>6</sub>:  $A = 6.5$ ,  $C = 12.6$  (in arbitrary units),  $\lambda_0 = 1787.45$  Å and  $\Delta = 0.88$  Å (27.5 cm<sup>-1</sup>).

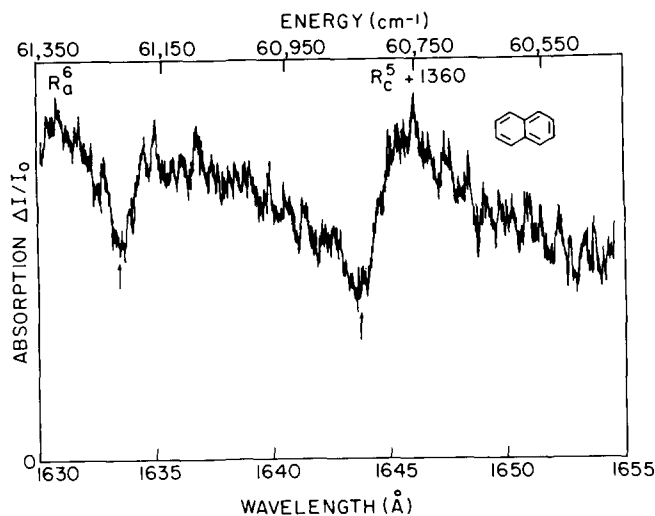


FIG. 2. The absorption spectra of naphthalene in pulsed planar expansions of Ar ( $p = 105$  Torr) in the region 1630–1650 Å. The spectral resolution is 0.5 Å. The antiresonances corresponding to the  $R_e^5 + 1360$  and to the  $R_a^6$  Rydberg states (according to the assignment of Refs. 15 and 19) are marked by arrows.

room temperature value  $\Gamma = 75 \text{ cm}^{-1}$ ,<sup>15,19</sup> whereupon the excessive homogeneous broadening make the thermal congestion effects. Our spectroscopic approach can readily be extended throughout the LiF region (up to 11 eV) and will contribute towards the elucidation of the microscopic aspects of intramolecular dynamics and photochemistry.

### Third-order MBPT gradients<sup>a)</sup>

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Many-body perturbation theory (MBPT) and its infinite-order coupled-cluster (CC) extensions have been demonstrated to be powerful methods for the accurate inclusion of electron correlation in *ab initio* quantum chemistry applications.<sup>1</sup> However, the study of potential energy surfaces also requires a convenient method of identifying extremum points. Analytical gradient methods have been developed for this purpose for the SCF, MCSCF, and CI approximations.<sup>2</sup> Previous MBPT gradient studies have been limited to second order.<sup>3</sup> In this letter we report the first third-order MBPT and partial fourth-order D-MBPT(4) analytical gradient calculations.

The detailed equations are presented elsewhere,<sup>4</sup> derived from iteration of the CC equations. An alternative derivation of MBPT(3) gradient equations was presented by Jørgensen and Simons.<sup>5</sup> In our approach, for each degree of freedom,

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$$\frac{\partial E_3}{\partial X} = \mathcal{E}_3 = \sum_{i>j} \sum_{a>b} [\langle ab || ij \rangle \Delta t_{ij}^{ab}(2) + \langle ab || ij \rangle \Delta \tau_{ij}^{ab}(2)],$$

where  $\Delta \tau(2)$  and  $\Delta t(2)$  are defined below;  $\langle ab || ij \rangle$  is the transformed two-electron integral ( $i, j, k, \dots$  are occupied in the SCF reference and  $a, b, c, \dots$  are unoccupied); and  $\langle ab || ij \rangle$  is the complete derivative of the two-electron integral, i.e., it includes both orbital modifications due to the changes in the primitive basis sets and in the linear MO coefficients. Using script to indicate derivative quantities, we have,

$$\Delta t_{ij}^{ab}(2) = L_{ij}^{ab}[t(1)]/D_{ij}^{ab}, \quad (2)$$

$$\Delta \tau_{ij}^{ab}(2) = \{\mathcal{F}_{ij}^{ab}[\Delta t(2)] + \mathcal{L}_{ij}^{ab}[t(1)] + L_{ij}^{ab}[\tau(1)]\}/D_{ij}^{ab}, \quad (3)$$