Resonance-enhanced Multiphoton Ionization Spectroscopy of the S_1–S_0 Transition of Benzo[*e*]pyrene for Real-time Analysis

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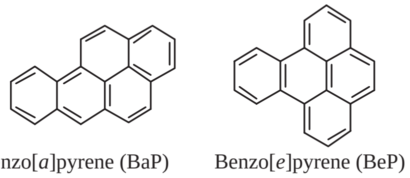
The electronic spectrum of benzo[*e*]pyrene (BeP) was recorded using resonance-enhanced multi-photon ionization (REMPI) spectroscopy. A number of bands were observed and assigned to the origin band and vibronic bands of the S_1–S_0 transition. Ab initio calculations were performed to assign the vibrational structures in S_1. The origin band of BeP is well separated in energy from the origin band of benzo[*a*]pyrene (BaP), an isomer of BeP, and so BeP and BaP can be readily distinguished by the REMPI method, despite having the same mass.

Benzo[*a*]pyrene (BaP) is one of the most hazardous carcinogenic compounds[1] emitted as a component of the exhaust gas from automobiles, incinerators, and so on. In contrast, benzo[*e*]pyrene (BeP), an isomer of BaP (Scheme 1), possesses virtually no such hazard. Thus, as the two molecules possess such different abilities to influence human health, it is essential that they are analyzed separately in measurements of exhaust gases. In addition, it is necessary to analyze exhaust gases in real-time because their composition and volume change dynamically in response to engine running conditions. Until recently, there has been no suitable method for the sensitive analysis of individual organic molecules in mixtures with sufficient time resolution to achieve real-time and on-line analysis. Conventional analysis for gaseous organic compounds can measure only the total hydrocarbon content (THC) when real-time measurements are required. The most sensitive and molecular-selective analytical method is gas chromatography/mass spectrometry (GC/MS) but this technique suffers from very low time resolution due to the need for sampling and pretreatment.

The supersonic jet resonance-enhanced multiphoton ionization (Jet-REMPI) method is likely to become one of the most important methods for high-sensitivity, molecular selective, and real-time analysis. REMPI is one of a number of possible multiphoton ionization processes induced by laser excitation. Ionization efficiency increases dramatically when the photon energy corresponds to the transition energy between the ground state S_0 and the excited state S_1 of the molecule. As all molecules have different ground and excited state energy levels, it is possible to select and analyze only a particular target compound from a mixture of gases by selecting the wavelength of the laser and the mass of the target compound. To use this method effectively, the resonance wavelengths of the excited states of target compounds must be known. The S_1 state of BaP has been previously recorded using laser-induced fluorescence excitation (LIF) and REMPI methods.[2] The S_1 0–0 band of BaP is 25233 cm^{-1} and other vibronic bands were also observed and assigned. On the other hand, there is no existing data on the excited states of BeP.


Benzo[*a*]pyrene (BaP) Benzo[*e*]pyrene (BeP)

Scheme 1. Structures of BaP and BeP.

In this study, we recorded the electronic spectrum of BeP using a Jet-REMPI method to provide information on the excited state of BeP and to confirm the capability of the Jet-REMPI method for molecule selective and real-time analysis.

The experimental apparatus has been described previously.[3] The sample BeP was purchased from Tokyo Chemical Industry Co., Ltd., and was used without further purification. The sample was introduced into the vacuum chamber continuously through a 100 µm pinhole nozzle and seeded in room air. The sample lines and the nozzle were heated to 200 °C. A frequency-doubled dye laser (Spectra Physics: Sirah Cobra-Stretch) pumped by the third harmonic of a Nd^{3+}:YAG laser (Spectra Physics: INDI-HG20) was operated at 20 Hz. The laser beam was focused onto a sample jet with a lens of focal length 300 mm. The ions produced by the laser ionization were introduced into a linear time-of-flight mass spectrometer with customized ion electrodes and detected by a Daly-type detector. The detected signal was amplified by a preamplifier (NF Electronics: BX31A) and recorded using a digital oscilloscope (IWATSU: DS-4354ML). To measure the REMPI spectra, the intensity of signals at 252 mass units, assigned to BeP, were recorded as a function of the laser wavelength. There was no signal at heavier mass than the BeP monomer in the mass spectrum. It suggests spectral contamination from clusters can be negligible under the experimental condition. The high temperature of the nozzle may suppress cluster formation.

All calculations were performed using the Gaussian 03 series of programs.[4] The equilibrium geometry and frequencies of BeP were determined using the B3LYP/6-311G(d,p) basis set for the ground state and CIS/6-311G(d,p) basis set for the S_1 state.

Figure 1 shows the REMPI spectrum of BeP between 26700 and 28500 cm^{-1}. The spectrum contains a large number of bands, with the lowest energy band at 26974 cm^{-1} being assigned to the origin of the S_1–S_0 transition. Some of the other observed bands are assigned tentatively to transitions to vibronically excited states of BeP using the results of quantum calculations, and are listed in Table 1. BeP possesses C_{2v} symmetry,

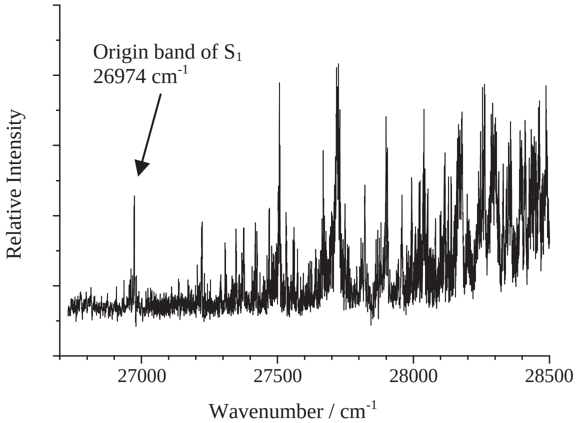


Figure 1. REMPI spectrum of BeP between 26700 and 28500 cm^{-1}.

Table 1. Experimental and calculated frequencies of BeP in the S_1 state

Exp./cm^{-1}	Vibrational shift/cm^{-1}	Cal./cm^{-1}	Assignment
26974	0		
27223	249	242	v_6 b_2
27309	335	323	v_9 a_1
27348	374	363	v_{10} a_1
27377	403	391	v_{11} b_2
27419	445	433	v_{14} a_1
27470	496	484	v_{16} b_2
27508	534	521	v_{19} a_1
27532	558	542	v_{21} b_2
27561	587	585	v_{22} b_2
27668	694	680	v_{26} b_2
27720	747	722	v_{29} a_1
		740	v_{31} b_2
27821	847	828	v_{35} a_1
27900	926	899	v_{39} b_2
27956	982	949	v_{43} b_2

so all 90 vibrational modes were classified as one of the 4 irreducible representations; a_1, a_2, b_1, and b_2. All the observed bands were assigned to the a_1 or b_2 symmetries. Both the ground state S_0 and the excited state S_1 have the same symmetry $^1A_1$. According to the selection rule for photon absorption, only the a_1 symmetry is allowed for the vibronic excitation from S_0 to S_1. The observed bands cannot be assigned using only a_1 symmetry. It suggests the existence of vibronic coupling with the higher excited state such as S_2. The excited state S_2 has $^1B_2$ symmetry, so S_1 vibrations in b_2 symmetry can appear by the intensity borrowing from S_2. Previous experiments have recorded the electronic spectra of BeP in solution, and have found the S_1 state at 3.37 eV and the S_2 state at 3.73 eV.[5] Furthermore, we calculated the S_1 and S_2 energy separation from S_0 using SAC-CI/cc-pVDZ. The calculated energy of S_1 is 3.35 eV and of S_2 is 3.94 eV. In the case of the molecule, dibenzofuran, it is believed that there is a perturbation from S_2 in the S_1–S_0 transition due to a small energy gap between the S_2 and S_1 states.[6] Given the small energy gap between S_2 and S_1 in BeP, it is reasonable to assume that the additional bands observed arise from a similar S_2 perturbation. The peak at 27720 cm^{-1} is believed to be broad owing to the presence of overlapping components, which are tentatively assigned to v_{29} (a_1) and v_{31} (b_2).

In the REMPI spectrum, the background intensity of the spectrum increases from around the 28000 cm^{-1} energy region. This is due to nonresonance multiphoton ionization. The ionization potential of BeP is about 7.43 eV (59900 cm^{-1}).[7] Near the region of the origin band, the transition energy is 26974 cm^{-1} and 3 photons are required for ionization. As the wavelength of the laser decreases and the photon energy increases, the 2-photon energy of the laser comes close to the ionization potential. In the case of 2-photon ionization, lower laser powers are required for nonresonant ionization than in the case of 3-photon ionization. Therefore, 2-photon nonresonant ionization begins to occur in the higher energy region, leading to an increase in the intensity of the background signal.

For analyzing BaP and BeP in a mixture using the REMPI method, it is necessary to distinguish between the isomers by the wavelength of their electronic excitation. The origin band of BeP is at 26974 cm^{-1} from this REMPI spectrum and the origin band of BaP is at 25233 cm^{-1}.[2] The difference of these two bands is about 1700 cm^{-1}, meaning that the two compounds can be analyzed individually in a mixture by selecting the appropriate laser wavelength.

In conclusion, the electronic spectrum of BeP was observed for the first time using the REMPI method, and the origin and vibronic bands of the S_1 excited states were assigned tentatively by comparison with the results of quantum chemical calculations. The energy of the origin band of BeP is quite distinct from that of BaP, so BeP and BaP can be analyzed individually in a mixture very effectively using the REMPI method. To confirm the vibrational assignments, dispersed fluorescence spectroscopy of jet-cooled BeP are now in progress.

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