Inelastic X-ray scattering in molecular liquids and electron correlation effects

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Inelastic X-ray scattering spectra of liquid water and cyclohexane have been measured with 2 eV resolution for a momentum transfer range between 0.69 and 2.77 au at BL16A of the Photon Factory, KEK, Tsukuba. Observed spectra are transformed to the dynamic structure factor which is normalized by using the Bethe sum rule, and the static structure factor is obtained. From a comparison with extended CI calculations by the use of various basis sets, correlation effects are proved to be of vital importance in inelastic X-ray scattering.

Keywords: inelastic X-ray scattering; molecular liquids; dynamic structure factor; static structure factor; electron correlations.

1. Introduction

Inelastic X-ray scattering (IXS) spectra have been known to be a source of various information on electronic states of matters. The double differential cross section of IXS is expressed by the dynamic structure factor $S(\mathbf{q},E)$ where momentum, $\mathbf{q}$, and energy, E, are transferred (Schulke, 1991),

$$(\partial^2 \sigma / \partial \Omega \partial E) = (\partial \sigma / \partial \Omega)_{Th} S(\mathbf{q}, E). \quad (1)$$

Here, $(\partial \sigma / \partial \Omega)_{Th}$ is the Thomson-scattering cross section. $S(\mathbf{q},E)$ is related to the dielectric response function (Schulke, 1991), and hence various properties of materials such as reflectance, stopping power, mean excitation energy and so on can be extracted (Inokuti, 1971; Williams *et al.*, 1991). In particular, it is known that the static structure factor $S(q)$ derived from $S(\mathbf{q},E)$ is a very correlation-sensitive quantity (Meyer *et al.*, 1995*a*,*b*). Although
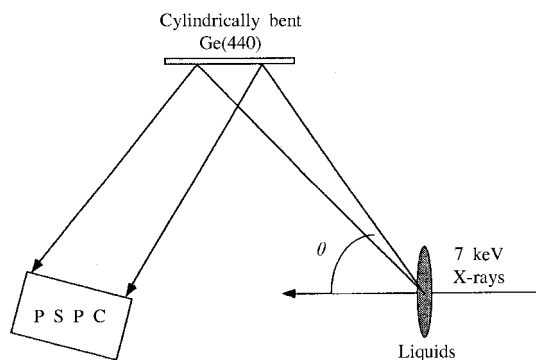
these properties can also be obtained by using EELS, the IXS method has several experimental advantages: it is free from various problems with which EELS is plagued, *e.g.* multiple scattering, a need of a vacuum, and charge-up phenomena.

So far, IXS spectra have been reported mainly for elementary solids like Li (Schulke, 1991), because of extremely small cross sections of IXS, especially at small *q*. Recent developments of synchrotron radiation sources, however, have made it possible to extend IXS spectroscopy to compounds (Watanabe, Hayashi & Udagawa, 1997). Molecules which consist of a limited number of atoms allow us to use accurate *ab initio* wave functions to compare theoretical calculations with experimental data. In this study, IXS spectra of water and cyclohexane have been obtained over a momentum transfer range between 0.69 and 2.77 au and compared with Compton profiles. $S(q)$ of water is calculated with various wave functions including electron correlation effects, and basis set dependency is discussed.

2. Experimental

IXS measurements were carried out at a multipole wiggler line, BL16A, of the Photon Factory, KEK, Tsukuba (Matsushita *et al.*, 1989). The incident X-rays were focused to a liquid jet expanded from a nozzle at the centre of a chamber filled with He gas; no liquid cell was used to avoid scattering from window materials. The scattered X-rays were vertically focused and horizontally
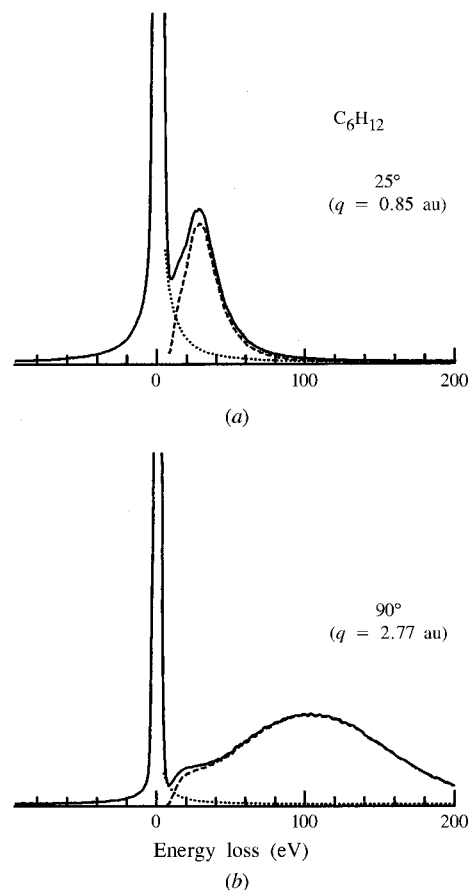
Figure 1
Schematic experimental set-up.

Figure 2
IXS spectra of cyclohexane obtained at scattering angles of 25 and 90° before (solid line) and after (chain) subtraction of the elastic scattering (dots).

dispersed with respect to the scattering plane by a cylindrically bent Ge(440) crystal having a 550 mm radius of curvature, and detected with a 100 mm long position-sensitive proportional counter (PSPC), as is schematically shown in Fig. 1. In this configuration the energy resolution is determined by the illuminated sample volume and was $\sim$2 eV at 7.3 keV from the FWHM of the elastic scattering line. By varying the scattering angle from 20 to 90°, a momentum transfer range $0.69 \leq q \leq 2.77$ au is covered. The measured spectra were analyzed in a similar manner as described previously (Watanabe, Hayashi & Udagawa, 1997).

3. Results and discussion

3.1. Dynamic structure factor S(q,E)

Fig. 2 shows IXS spectra of cyclohexane obtained at scattering angles of 25 and 90° before and after subtraction of the elastic scattering. IXS spectra are subsequently transformed to $S(q,E)$, which is shown in Fig. 3, by the use of the Bethe sum rule. Here, $S(q,E)$ is spherically averaged owing to random orientation of molecules in liquids. It has been known that the impulse
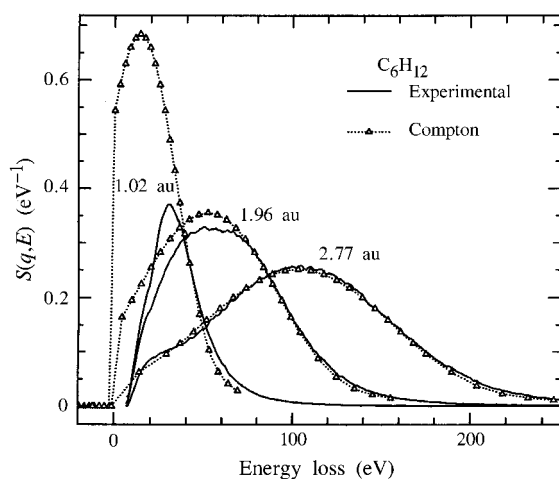

Figure 3
Comparisons of observed $S(q,E)$ of cyclohexane with those calculated from Compton profiles.
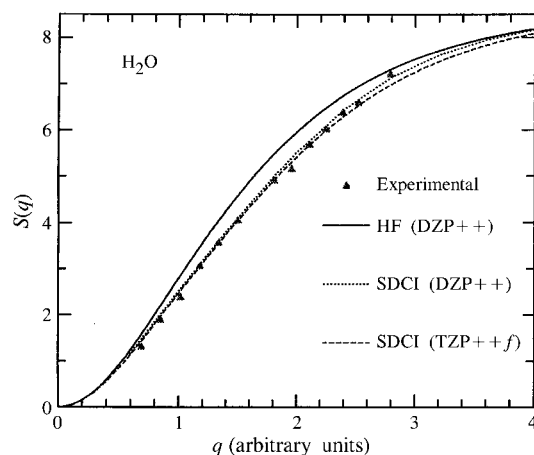

Figure 4
Comparison of the observed $S(q)$ of water with those calculated by various approximations. Full line, dotted line: Wang *et al.* (1994); dashed line: Watanabe, Hayashi & Udagawa (1997).

approximation is valid at large q, and in that case IXS can be analyzed as Compton scattering (Epstein, 1977). Eisenberger & Marra (1971) have experimentally shown that the Compton profiles of individual bonds are transferable among various hydrocarbons and tabulated those for C—H, C—C and C═C. Thus, it is possible to compare the observed $S(q,E)$ with the Compton profiles about C_6H_{12}. In Fig. 3, calculated Compton profiles are compared with the observed $S(q,E)$. At the highest q studied here, namely 2.77 au, the two coincide within 1.1×10^{-2} eV^{-1} except for a shoulder portion at $E \simeq 20$ eV in the observed $S(q,E)$. This indicates that the impulse approximation holds at $q = 2.77$ au and also demonstrates the accuracy of the present experiment. With decrease in q, the observed $S(q,E)$ deviates from calculated ones as expected.

3.2. Static structure factor S(q)

The static structure factor can be derived from $S(q) = \int S(q,E)\,\mathrm{d}E$ and is shown in Fig. 4 for water. Since 1 s contributions are out of the range of the present measurement, calculated values according to Thakker & Smith's (1978) formula are added in order to make comparisons with theoretical calculations. Because the core contributions are small over the present q–E range, any error in the estimate of the core contribution is not significant.

It has already been confirmed that calculations by assuming an independent atom model (IAM), which is conventionally employed in analyzing X-ray diffraction, always overestimates $S(q)$ significantly even though correlated wave functions are used (Watanabe, Hayashi & Udagawa, 1997). Wang *et al.* (1994) have recently carried out $S(q)$ calculations on a series of ten electron molecules, including H_2O, by using double zeta augmented with both polarization and the diffuse functions (DZP++) for molecular HF as well as CI including all single and double excitations (SDCI). Their results are also shown in Fig. 4, which demonstrates that the SDCI calculation shows a significant improvement and that electron correlation effects are of vital importance in IXS.

We (Watanabe, Hayashi, Udagawa *et al.*, 1997) have also developed a computer code to calculate $S(q)$ at the SDCI level with larger basis functions. Calculations were carried out by the use of triple zeta plus polarization augmented with diffuse and f-polarization functions (TZP++f). They are also shown in Fig. 4. Although TZP++f gives a slightly smaller $S(q)$ than DZP++ at $q > 2$ au, the differences are comparable with experimental errors. Thus, the size of basis sets used in this study is concluded to be large enough to predict the inelastic scattering intensities of H_2O. A further effort to extend the calculation to larger molecules is now in progress.

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