

## Atomic decomposition of carbonyl stretching IR absorption intensities

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### INTRODUCTION

The description of a molecular property in terms of its constituent parts, the atoms, is the ultimate desire of almost all chemists. In this work, we report an atomic decomposition of infrared intensities for the carbonyl stretch in a set of several mono and dicarbonyl compounds, looking for trends in their contributions and novel interpretations of the vibrational phenomena.

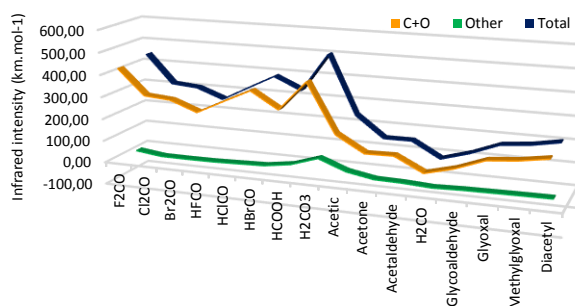
### METHODOLOGY

The general methodology is described in recent reports<sup>1</sup> and is essentially a matrix transformation from the APT's Cartesian space to the normal coordinate space, for each atom in the molecule individually. This transformation yields  $N$  (the number of atoms) terms which can be related with effective charges. Those terms can be evaluated for each vibrational mode as well for the sum of all modes, being in this case closely related with the Crawford's  $G$  Sum Rule<sup>2</sup>.

### RESULTS

**Table 1.** Atomic contributions to the intensities plus their percentages of the total intensity.

Molecule	km.mol <sup>-1</sup>		%	
	C	O	C	O
F <sub>2</sub> CO	337.0	89.6	76.2	20.3
Cl <sub>2</sub> CO	208.6	104.8	66.4	33.4
Br <sub>2</sub> CO	192.3	111.5	63.3	36.7
HFCO	184.3	74.8	70.9	28.8
HCICO	209.4	109.2	64.8	33.8
HBrCO	242.2	133.8	62.9	34.8
HCOOH	211.9	91.7	64.1	27.7
H <sub>2</sub> CO <sub>3</sub>	323.7	110.6	64.5	22.0
CH <sub>3</sub> COOH	186.4	84.3	63.4	28.7
Acetone	94.6	54.7	63.6	36.8
Acetaldehyde	97.6	54.7	65.3	36.6
Formaldehyde	56.7	34.4	69.9	42.3
Glycoaldehyde	77.2	46.7	65.2	39.5
Glyoxal	99.6	71.8	59.4	42.8
Methylglyoxal	108.6	74.9	60.3	41.6
Diacetyl	123.7	80.4	60.7	39.5



**Figure 1.** Carbon and oxygen intensities versus the total intensities of the mode (blue).

It is easily seen that almost all the infrared intensity of the carbonyl stretch is concentrated on the carbon and oxygen atoms. Figure 1 makes it very clear since the yellow line, representing the sum of the carbon and oxygen intensities closely follows the blue line (the total intensity). The green line, representing all the intensity allocated on the “other” atoms (all the atoms but C or O) is near zero in all cases except for the acids, where there is a reasonable concentration of intensities on the acidic hydrogens.

### CONCLUSIONS

One can conclude that the atomic contributions to infrared intensities provide a very useful tool for interpreting vibrational phenomena. Even though the values of the contributions vary in a wide range for both carbon and oxygen atoms among the molecules, their proportions to the total intensity are remarkably constant; moreover, almost all the intensity is concentrated on these two atoms. These observations are general and the values of the proportions are just slightly affected by the chemical groups attached to the carbonyl in a way somewhat related to the electronegativity of those groups.

### ACKNOWLEDGEMENTS

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<sup>1</sup> AF Silva, WE Richter, RE Bruns, *PCCP*, submitted.

<sup>2</sup> WT King, GB Mast, PP Blanchette. *JCP* 56, 4440 (1972).